JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

1913. Vol. CIV. Part I.

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C.
1913.

Richard Clay & Sons, Limited,
BRUNSWICK STREET, STAMFORD STREET, S.E.,
AND BUNGAY, SUFFOLK.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Preparation of $\Delta^{\alpha\gamma}$-Butadiene and its Homologues. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252499).—When hydrogenated hydrocarbons of the benzene series containing at least one double bond are heated at high temperatures at the ordinary or (preferably) reduced pressures with an indifferent gas (such as nitrogen), they yield derivatives of butadiene. Isoprene is thus obtained from the lower-boiling fractions furnished by the decomposition of 1-methyl-Δ^1-*cyclo*hexene, or of 1-methyl*cyclo*hexan-2-ol, whilst *cyclo*hexene yields $\Delta^{\alpha\gamma}$-butadiene (erythrene), and 1-methyl-Δ^2-*cyclo*pentene furnishes piperylene, $CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH_2$. F. M. G. M.

Preparation of Isoprene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251216).—When *as*-dimethylallene (b. p. 39—41°) is dropped on to strongly heated aluminium oxide, preferably under a pressure of about 20—30 mm., it is converted into pure isoprene; the aluminium oxide can be replaced by other catalytic agents, and the formation of higher polymerides must be avoided. F. M. G. M.

Preparation of $\beta\gamma$-Dimethylerythrene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 253081. Compare A., 1912, i, 741).—The preparation of $\beta\gamma$-dimethylerythrene by heating pinacone (1 part) with dilute sulphuric acid (10 parts) is described in the literature; it is now found that the most favourable proportions are 1 part of sulphuric acid (20%) to 10,000 parts of pinacone heated at 130—140°,

when a yield of over 70% of $\beta\gamma$-dimethylerythrene is obtained. The sulphuric acid can be replaced by methanedisulphonic or naphthalene 1 : 5-disulphonic acid. F. M. G. M.

The History of Distillation and of Alcohol. HERMANN SCHELENZ (*Zeitsch. angew. Chem.*, 1912, **25**, 2526—2527).—Polemical against von Lippmann (A., 1912, i, 824 ; ii, 897). C. H. D.

Preparation of Homologues of Pinacone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 251330, 251331).—The homologues of pinacone can be readily prepared in satisfactory yield by the action of aluminium amalgam on the homologues of acetone.

$\gamma\delta$-*Diethylhexane*-$\gamma\delta$-*diol*, $OH\cdot CEt_2\cdot CEt_2\cdot OH$, m. p. 27—28°, b. p. 116—119°/17 mm., is thus obtained from diethyl ketone. $\gamma\delta$-*Dimethylhexane*-$\gamma\delta$-*diol*, $OH\cdot CMeEt\cdot CMeEt\cdot OH$, b. p. 78—79°/3 mm., is prepared from methyl ethyl ketone, whilst methyl propyl ketone furnishes $\delta\epsilon$-*dimethyloctane*-$\delta\epsilon$-*diol*, $OH\cdot CMePr^{a}\cdot CMePr^{a}\cdot OH$, m. p. 35°, b. p. 116—170°/15 mm. These reactions can be carried out in either benzene or carbon tetrachloride solutions.

II. States that magnesium and mercuric chloride in the presence of cuprous chloride can replace the aluminium amalgam in these preparations. F. M. G. M.

The Formation of Polyatomic Rings. ADOLF FRANKE and O. KIENBERGER (*Monatsh.*, 1912, **33**, 1189—1203).—In a repetition of the work of Alberti and Smieciuszewski (A., 1906, i, 619) the authors converted $\alpha\kappa$-dihydroxydecane into the chlorohydrin, but found that the product contained also about 15% of the corresponding dichloride, and that the mixture could not be satisfactorily separated; the constitution of the chlorohydrin was proved by re-conversion into the glycol. Heating the impure chlorohydrin with sodium hydroxide and sand gave rise to a mixture of substances of high molecular weight, but no indication of the heterocyclic isomerides, $C_{10}H_{20}O$, described earlier (*loc. cit.*).

Endeavours to prepare cyclic molecules from $\alpha\kappa$-dibromodecane (Franke and Hankam, A., 1910, i, 460) by the action of ordinary zinc dust in aqueous alcohol produced *n*-decyl alcohol, whilst the action of sodium in ether gave *n*-decane, together with a *substance*, $C_{20}H_{40}$ or $C_{20}H_{42}$, silky needles, m. p. 36°. D. F. T.

Halogen Ethers. A. KARVONEN (*Chem. Zentr.*, 1912, ii, 1266—1267; from *Acad. Sci. Fennicae.*, *A*, 3, 1—103. Compare A., 1909, i, 202).—The boiling points and densities have been determined for a number of carefully purified halogen ethers of the series $RO\cdot CH_2X$, $RO\cdot CH_2\cdot CH_2X$, and $RO\cdot CH_2\cdot CH_2\cdot CH_2X$, where R = H, Me, Et or Pr, and X = Cl, Br or I. They have been compared with some ethylene- and trimethylene-halogen hydrins, and with some simple alkyl haloids.

In the case of metameric halogen ethers, the removal of the halogen atom from the oxygen atom frequently causes a lowering of the boiling point, but as the molecule becomes more symmetrical with regard to the groups R and $(CH_2)_nX$, the boiling point rises. As the distance

of the halogen atom from the oxygen atom increases, the differences between the boiling points of the chloro- and bromo- and bromo- and iodo-compounds diminish. The difference between the boiling points of the methyl and ethyl members of a homologous series is less than that between the ethyl and propyl members. The boiling points of halogen ethers with three, four, and five members in the chain are higher than those of the corresponding alkyl haloids, but with six members in the chain the ethers boil at a lower point. The hydrins boil at higher temperatures than the halogen ethers. As for the densities, the removal of the halogen atom from the oxygen atom causes an increase in density, and the halogen ethers take a mean place between the hydrins and the alkyl haloids. In general, the simultaneous separation of two negative substituents in the molecule causes an increase in density.

General methods for the preparation and purification of these compounds are discussed. The α-halogen ethers were usually prepared by the action of the hydrogen haloid on a mixture of the alcohol with trioxymethylene (compare Litterscheid, A., 1904, i, 364); the β-chloro- and bromo-ethers by the action of the phosphorus haloid on alkyloxylated alcohols, and the γ-ethers by the action of alcohols or alcoholates on alkylene haloids, the halogenating of ethers, or by the transformation of ethers into one another. The halogen ethers are all colourless, mobile liquids. The α-ethers have pungent, aldehydic odours and fume in the air, but the β- and γ-ethers are agreeable.

The following compounds are described:

A. *α-Halogen Ethers.*—Chloromethyl ether, b. p. 59·1°/766 mm., gives a *pyridine* compound, $Py,CH_2Cl{\cdot}OMe$, colourless, hygroscopic tablets; *platinichloride*, $(Py,CH_2Cl{\cdot}OMe)_2PtCl_4$, reddish-yellow needles, m. p. 189°. Bromomethyl ether, b. p. 87·2°/746 mm.; *pyridine* compound, $Py,CH_2Br{\cdot}OMe$, very hygroscopic powder. Iodomethyl ether, b. p. 25°/13 mm. Chloromethyl ethyl ether, b. p. 83°/763·1 mm.; *pyridine* compound, $Py,CH_2Cl{\cdot}OEt$, colourless, hygroscopic tablets; *platinichloride*, $(Py,CH_2Cl{\cdot}OEt)_2PtCl_4$, reddish yellow prisms, m. p. 182°. *Bromomethyl ethyl ether*,

$$OEt{\cdot}CH_2Br,$$

from ethyl alcohol, trioxymethylene, and hydrogen bromide, b. p. 92·2°/745·7 mm.; *pyridine* compound, $Py,CH_2Br{\cdot}OEt$, white, hygroscopic. *Iodomethyl ethyl ether*, $OEt{\cdot}CH_2I$, with hydrogen iodide, b. p. 31°/11 mm.; *pyridine* compound, $Py,CH_2I{\cdot}OEt$, colourless, hygroscopic. Chloromethyl propyl ether, b. p. 109°/759·7 mm.; *pyridine* compound, $Py,CH_2Cl{\cdot}OPr$, colourless, very hygroscopic; *platinichloride*, $(Py,CH_2Cl{\cdot}OPr)_2PtCl_4$, m. p. 185°. *Bromomethyl propyl ether*, $OPr{\cdot}CH_2Br$, from normal propyl alcohol, trioxymethylene, and hydrogen bromide, b. p. 133·9°/744·4 mm.; *pyridine* compound,

$$Py,CH_2Br{\cdot}OPr,$$

colourless, hygroscopic lamellæ. *Iodomethyl propyl ether*, $OPr{\cdot}CH_2I$, with hydrogen iodide, b. p. 39°/5 mm.; *pyridine* compound,

$$Py,CH_2I{\cdot}OPr,$$

colourless.

B. *β-Halogen Ethers.*—Methyl β-chloroethyl ether,

$$OMe{\cdot}CH_2{\cdot}CH_2Cl,$$

by the action of phosphorus pentachloride on ethylene glycol monomethyl ether, $OMe\cdot CH_2\cdot CH_2\cdot OH$, and not by Fileti and Gaspari's method, b. p. 89·4°/763·3 mm. *Methyl β-bromoethyl ether*, $OMe\cdot CH_2\cdot CH_2Br$, from methyl β-iodoethyl ether and bromine, b. p. 110·3°/759·4 mm. Methyl β-iodoethyl ether (A., 1909, i, 202), $D_4^{20} = 1·8241$. Ethyl β-chloroethyl ether, from ethylene glycol monoethyl ether and phosphorus trichloride, b. p. 107°/751·8 mm. Ethyl β-bromoethyl ether, b. p. 40°/24 mm., from ethyl β-iodoethyl ether (*ibid.*). Propyl β-chloroethyl ether, from ethylene glycol monopropyl ether and phosphorus pentachloride, b. p. 130°/756·3 mm. *Propyl β-bromoethyl ether*, $OPr\cdot CH_2\cdot CH_2Br$, from ethylene glycol monopropyl ether and phosphorus tribromide or hydrogen bromide, b. p. 149°/757·8 mm., 4? 11 mm. Propyl β-iodoethyl ether, $D_4^{20} = 1·5464$ (*ibid.*).

C. *γ-Halogen Ethers*.—Methyl γ-chloropropyl ether, b. p. 110·4 756·6 mm. *Methyl γ-bromopropyl ether*, $OMe\cdot[CH_2]_3\cdot Br$, from trimethylene bromide, methyl alcohol, and zinc oxide, b. p. 13? 764·4 mm. *Methyl γ-iodopropyl ether*, $OMe\cdot[CH_2]_3\cdot I$, from the chloro-ether and calcium iodide, b. p. 158—158·5°/761·8 mm. Ethyl γ-chloropropyl ether, b. p. 129°/754·7 mm. Ethyl γ-bromopropyl ether, by Noyes's method (A., 1898, i, 59), b. p. 147·8°/750 mm. *Ethyl γ-iodopropyl ether*, $OEt\cdot[CH_2]_3\cdot I$, from the chloro-ether and calcium iodide, b. p. 172·5°/778·7 mm.

D. *Halogen Hydrins and Alkyl Haloids*.—Ethylene chlorohydrin, $OH\cdot CH_2\cdot CH_2Cl$, from ethylene glycol and hydrogen chloride, b. p. 129·5°/761·1 mm. Ethylene bromohydrin, $OH\cdot CH_2\cdot CH_2Br$, with hydrogen bromide, b. p. 45·6°/11 mm. Ethylene iodohydrin,

$$OH\cdot CH_2\cdot CH_2I,$$

from the chlorohydrin and sodium iodide, b. p. 61°/7 mm. Trimethylene chlorohydrin, $HO\cdot CH_2\cdot CH_2\cdot CH_2Cl$, from trimethylene glycol and hydrogen chloride, b. p. 160°/734·1 mm. Trimethylene bromohydrin, $HO\cdot CH_2\cdot CH_2\cdot CH_2Br$, b. p. 62°/5 mm. Trimethylene iodohydrin, $HO\cdot CH_2\cdot CH_2\cdot CH_2I$, b. p. 88°/4 mm.

n-Propyl chloride, b. p. 46·6°/770·5 mm.; *n*-propyl bromide, b. p. 70·8°/769·2 mm.; *n*-propyl iodide, b. p. 101·9°/765·5 mm. *n*-Butyl chloride, b. p. 77·8°/762·7 mm.; *n*-butyl bromide, b. p. 100·? 745·6 mm.; *n*-butyl iodide, b. p. 129·4°/746·4 mm. *n*-Amyl chloride, b. p. 105·7°/759·3 mm.; *n*-amyl bromide, b. p. 127·9°/762·4 mm.; *n*-amyl iodide, b. p. 35°/7 mm. *n*-Hexyl chloride, b. p. 13?·? 764·7 mm.; *n*-hexyl bromide, b. p. 153·4°/766·3 mm.; *n*-hexyl iodide, b. p. 51°/6 mm. J. C. W.

Preparation of Carbonic Esters. RUDOLF SCHEUBLE and A. HOCHSTETTER (D.R.-P. 252758).—*Glyceryl carbonate*, m. p. 14?, crystallises from pyridine, and is obtained in theoretical yield when anhydrous glycerol (2 parts) is heated at 140° with phenyl carbonate (7 parts) and the phenol subsequently removed in a vacuum; in this case the glycerol is fully esterified. When twice this proportion of glycerol is employed and the product extracted with a small quantity of acetone, any of the foregoing ester is left insoluble, and the acetone furnishes a complicated mixture of esters in which the glycerol is not fully esterified. These compounds can also be prepared by the action

of ethyl carbonate or carbonyl chloride on glycerol dissolved in an indifferent acid absorbing medium, and find employment in pharmacy.

F. M. G. M.

Preparation of Halogen Formyl Esters. EMANUEL MERCK (D.R.-P. 251805. Compare A., 1912, i, 877).—Chloroformyl esters can be obtained by the interaction of hydroxy-compounds with carbonyl chloride in the presence of an indifferent base or acid absorbent: $R\cdot OH + COCl_2 = RO\cdot COCl + HCl$.

Methylhexylcarbinyl chloroformate, a colourless oil, b. p. 75°/6 mm., is obtained when a cooled benzene solution of methylhexylcarbinol (130 parts) is treated with carbonyl chloride with the subsequent slow addition of pyridine (79 parts) dissolved in 500 parts of benzene; when treated with ammonium hydroxide, it furnishes the corresponding known carbamyl ester (m. p. over 55°).

Thymyl chloroformate has b. p. 106°/10 mm., and menthyl chloroformate, b. p. 96°/5 mm.

Ethyl bromoformate, an oil with a characteristic odour, b. p. 132°/760 mm. with partial decomposition, is obtained from carbonyl bromide and ethyl alcohol in absolute ethereal solution in the presence of quinoline, whilst ethyl chloroformate is analogously prepared in the presence of methylaniline.

F. M. G. M.

Preparation of Esters of Butenol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 252160).—When $\Delta^{\alpha\gamma}$-butadienes of the general formula $CH_2{:}CR\cdot CH{:}CH_2$ (where R is hydrogen or alkyl) are treated with a fatty acid in the presence of a condensing agent such as sulphuric acid, zinc chloride, or potassium hydrogen sulphate), they furnish esters which are readily purified, have a characteristic odour, and on hydrolysis yield the corresponding alcohol.

Methylbutyl acetate, an oil, b. p. 100° (about), D 0·870, and saponification number 418 (about), is obtained when isoprene (100 parts), acetic acid (300 parts), and concentrated sulphuric acid (1 part) are heated together during five hours at 50°.

F. M. G. M.

The Mercury Compounds of Ethyl Nitroacetate. W. PRAGER (*Monatsh.*, 1912, 33, 1285—1289).—The formation of ethyl mercuri-*aci*-nitroacetate anhydride, $O{<}{}^{NO}_{Hg}{>}C\cdot CO_2Et$, from the interaction of ammonium *aci*-nitroacetate and mercuric chloride (Scholl and Nyberg, A., 1906, i, 563), is probably preceded by the formation of a compound, $CO_2Et\cdot CH{:}NO_2\cdot HgCl$, ethyl mercuri-*aci*-nitroacetate chloride, which, however, could not be isolated. In agreement with this idea, the yield of ethyl mercuri *aci*-nitroacetate is increased by the addition of an equivalent quantity of sodium acetate.

The solution of ethyl mercuri-*aci*-nitroacetate in sodium hydroxide solution contains *ethyl sodium mercuri*-aci-*nitroacetate hydroxide*,

$$CO_2Et\cdot C({:}NO_2Na)\cdot Hg\cdot OH,$$

which can be obtained as a greenish-yellow substance by evaporation with exclusion of atmospheric carbon dioxide. Ethyl mercuri-*aci*-

nitroacetate anhydride dissolves also in potassium cyanide solution, forming presumably the analogous *cyanide* compound,

$$CO_2Et\cdot C(:NO_2K)\cdot Hg\cdot CN.$$

Attempts to obtain substances of analogous structure to the above from nitroacetamide, dinitromethane, and ω-nitrotoluene produced only substances of the type $CHR:NO_2\cdot HgCl$; nitroacetamide gave a *substance*, $Hg(NH\cdot CO\cdot CH:NO_2\cdot HgCl)_2$; the potassium derivative of dinitromethane with mercuric chloride gave yellow needles of an explosive *substance*, $NO_2\cdot CH:NO_2\cdot HgCl$, together with an amorphous, yellow *substance* also containing chlorine. D. F. T.

Action of Aluminium Chloride on Acetic Anhydride. JACOB BÖESEKEN and MEYER CLUWEN (*Rec. trav. chim.*, 1912, 31, 367—369).—When acetic anhydride is added to warmed aluminium chloride, acetyl chloride distils off, leaving a heavy, white precipitate of aluminium monochlorodiacetate, which forms an *additive* compound with ether, $OEt_2,2AlCl(OAc)_2$, in large, limpid crystals. J. C. W.

Soaps. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1912, 26, 485—495. Compare Krafft and Stern, A., 1894, i, 439, 440; Krafft and Wiglow, A., 1896, i, 80; Krafft and Strutz, A., 1896, ii, 467; Krafft, A., 1899, ii, 471, 472, 473).—When sodium palmitate is crystallised from its aqueous solution, an acid soap separates, and the mother liquor becomes alkaline. Recalculation of the data given by Krafft shows that as the sodium palmitate solution decreases in concentration, so also does the concentration of sodium hydroxide in the mother liquor, the latter value, however, finally becoming constant. This is confirmed by experiments performed by the author, who, however, contrary to Krafft, finds that fatty acids are also retained in the mother liquors.

Krafft has shown that palmitic acid may be almost completely extracted from solutions of sodium palmitate by treatment with successive quantities of toluene. The author has performed a number of experiments on the quantitative extraction of the acid by a single treatment of aqueous solutions of sodium palmitate and oleate with measured amounts of toluene, and finds that the extractability depends both on the m. p. of the acid and on its solubility in toluene. The percentage of acid extracted is inversely proportional to the concentration of sodium hydroxide in the soap solution.

The bearing of the above results on the divergent action of soap is discussed, and the conclusion drawn that this action lies rather in the power of the soap solution to emulsify the grease than in the saponification of the latter by alkali. A partly rancid fat should thus be readily emulsified by a solution of soap of suitable concentration, whilst, on the other hand, a neutral fat would first acquire the necessary acidity by extraction of a portion of the acid from the soap solution. H. W.

Dissociation Constants of Aliphatic Hydroxy- and Alkyloxy-acids. MATTI H. PALOMAA (*Chem. Zentr.*, 1912, ii, 595—597; from *Ann. Acad. Sci. Fennicae*, 1911, *A*, 3, 1—34).—The dissociation constants of a number of aliphatic hydroxy- and alkyloxy-acids have been

determined with a view to ascertaining how this constant is affected by the positions of the oxygen atoms in the ·OH or ·OR group with respect to the carboxyl group. In general, the dissociation constant diminishes with increasing distance between the two groups, until in the δ-compounds it is nearly as low as in the normal fatty acids. Attempts to calculate the effect of distance on the specific influence of the ethereal oxygen atom by means of the equations $(y/y+2\cdot66)^{-x} = K_0^a/K_1^a$ and $(y/y+2\times2\cdot66)^{-x} = K_0^a/K_2^a$ showed that $x=2\cdot6$ in methoxy-compounds and 2·9 in ethoxy-compounds, the values of y being 1·45 and 1·78 respectively for the same compounds.

The following substances are described: n-*Butoxyacetic acid*, D_4^{15} 1·0256, D_4^{20} 1·0213, b. p. 113—116°/9—10 mm., K 0·0219, is a colourless liquid with a not unpleasant odour. iso*Butoxyacetic acid*, D_4^{15} 1·0117, D_4^{20} 1·0074, b. p. 114°/9 mm., K 0·0214, is a colourless liquid. *α-Ethoxypropionic acid*, b. p. 97°/11 mm., K 0·0246. *β-Methoxypropionic acid*, D_4^{15} 1·1064, D_4^{20} 1·1020, b. p. 107°/10 mm., K 0·00346. *β-Ethoxypropionic acid*, D_4^{15} 1·0508, D_4^{20} 1·0641, b. p. 119—120°/19 mm., K 0·00319. *δ-Methoxyvaleric acid*, D_4^{15} 1·0387, D_4^{20} 1·0344, b. p. 133—134°/13·5 mm., K 0·00191. T. A. H.

Action of Magnesium Methyl Iodide and Bromide on Di-α-bromo*iso*propyl Ketone and on α-Bromo*iso*propyl *tert.*-Butyl Ketone (Pentamethylbromoacetone): Synthesis of β-Hydroxy-pentamethyl-*n*-valeric Acid and Pentamethylvalerolactone. (Mlle.) A. Umnova (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1395—1406).—Instead of the expected methyldi*tert.*-butylcarbinol, the products of the interaction of di-α-bromo*iso*propyl ketone, magnesium methyl iodide, and water are: (1) *iso*propyl *tert.*-butyl ketone (compare Nef, A., 1900, i, 349), formed from the intermediate compound,

$$CMe_3\cdot CO\cdot CMe_2\cdot MgBr,$$

and (2) methyl*iso*propyl*tert.*-butylcarbinol (?), b. p. 65—75°/12 mm.

The action of magnesium methyl bromide on di-α-bromo*iso*propyl ketone yields the compound $CMe_3\cdot CMe(OMgBr)\cdot CMe_2\cdot MgBr$, the latter being converted by carbon dioxide into *β-hydroxy-ααβγγ-pentamethylvaleric acid*, $CMe_3\cdot CMe(OH)\cdot CMe_2\cdot CO_2H$, m. p. 128—129°, which has the normal molecular weight in boiling ether; the *silver* and *calcium* salts were analysed. Attempted oxidation of the sodium salt of the acid with potassium permanganate and subsequent distillation of the solution with sulphuric acid yields *ααββγ-pentamethylvalerolactone*, $CMe_2<\begin{matrix}CMe_2\cdot O\\ CMe_2\cdot CO\end{matrix}$, m. p. 59—60°, b. p. 215—220°, which has the normal molecular weight in freezing benzene; the formation of the lactone is shown to be due to the following isomeric change effected by the sulphuric acid: $CMe_3\cdot CMe(OH)\cdot CMe_2\cdot CO_2H \longrightarrow OH\cdot CMe_2\cdot CMe_2\cdot CMe_2\cdot CO_2H$. β-Hydroxy-ααββγ-pentamethylvaleric acid may also be obtained by the action of carbon dioxide and water on the product of the interaction of magnesium methyl iodide and α-bromo*iso*propyl *tert.*-butyl ketone. T. H. P.

Optically Active Dichlorosuccinic Acids. Bror Holmberg (*Svensk. Kem. Tid.*, 1912; Reprint, 6 pp.).—The dichlorosuccinic

anhydride obtained by the action of chlorine on a solution of maleic anhydride in carbon tetrachloride (compare Holmberg, A., 1911, i, 767; McKenzie, T., 1912, 101, 1196) is a mixture of a less soluble racemic dichlorosuccinic anhydride with a more soluble *meso*-anhydride in the approximate proportions 5 : 1. This behaviour is in marked contrast with the oxidation of maleic acid by potassium permanganate, when the sole product is *meso*-tartaric acid. The anhydrides on treatment with cold water gave the respective acids: r-*dichlorosuccinic acid*, tablets, m. p. 173—174° (decomp.); meso-*dichlorosuccinic acid*, prisms, m. p. 215° (decomp.).

By fractional recrystallisation of the salt of the racemic acid with *d*-α-phenylethylamine from warm water, there was obtained d-α-*phenylethylamine* d-*dichlorosuccinate*, m. p. 142—142·5°, from which the pure d-*dichlorosuccinic acid*, prisms, m. p. 164—165° (decomp.), $[\alpha]_D^{23}$ +80·4° (in ethyl acetate), could be separated by acidifying with sulphuric acid and extracting with ether. The mother liquor from the first crystallisation of the racemic salt contained a lævorotatory acid, which, when combined with *l*-phenylethylamine and crystallised from warm water, gave a salt of the same m. p. as that containing the *d*-acid and *d*-base; the acid isolated from this salt was pure l-*dichlorosuccinic acid*, m. p. 164—165°, $[\alpha]_D$ (in ethyl acetate) −80·38°.

The racemic acid, m. p. 173—174°, could be re-obtained by mixing equal amounts of these aenantiomorphs. D. F. T.

New Method of Preparation of Muconic Acid. ROBERT BEHREND and GERHARD TEN DOORNKAAT KOOLMAN (*Annalen*, 1912, 394, 228—247).—Malonic acid (2 mols.) and the sodium hydrogen sulphite compound of glyoxal are boiled with water for about an hour. The solution is evaporated to a syrup, which is boiled with glacial acetic acid for about six hours, and is then treated with 36% hydrochloric acid. The sodium chloride is removed, and the filtrate is evaporated with water to a syrup, which deposits crystals after one to two days. These are treated with 95% alcohol, collected, and crystallised from hot 80% alcohol. The product is the *lactone* of *sodium hydrogen β-hydroxy-γ-sulphoadipate*, $\begin{matrix} CO_2H\cdot CH_2\cdot CH\text{——}O \\ SO_3Na\cdot CH\cdot CH_2 \end{matrix}\!\!>\!CO,3\tfrac{1}{2}H_2O$, prismatic crystals, m. p. 270—272° (decomp.), occasionally melting at 80—85° in its water of crystallisation, re-solidifying, and melting again at 270—272°. The *lactone* of the corresponding potassium hydrogen salt, m. p. 262—264° (decomp.), is obtained in a similar manner. The *lactone* of the *sodium ethyl* salt, obtained from that of the sodium hydrogen salt, boiling 95% alcohol, and 1 drop of concentrated hydrochloric acid, forms long, felted needles containing H_2O, and has m. p. 145—147° (decomp.).

By heating on the water-bath for four hours with an alkali hydroxide and a little water, the lactone of sodium hydrogen hydroxysulphoadipate is decomposed, yielding, after solution in water and acidification, about 30% of muconic acid and 60% of succinic acid.

Muconic acid has m. p. 301—305° (decomp.), and is soluble in about 5000 parts of cold water and in about 100 parts of cold absolute alcohol.

A by-product in the preparation of the lactone is a *substance*, which is isolated as the amorphous *barium* salt, $C_{10}H_{14}O_{13}SBa_2$, from which muconic acid in a yield of 38%, but not succinic acid, can be obtained by heating with an alkali hydroxide and a little water on the water-bath.

For the preparation of muconic acid there is no need to isolate the lactone. Malonic acid and the sodium hydrogen sulphite compound of glyoxal are boiled with water for an hour, the solution is evaporated to a syrup, which is heated at 140—160° until gas almost ceases to be evolved, and is then treated with an alkali hydroxide and a little water on the water-bath, as above. C. S.

Elucidation of the Constitution of Cholic Acid by Bromination. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1912, **82**, 326—341).—On bromination of cholic acid, a brown, amorphous mass is obtained, which is decomposed by sodium hydroxide, losing part of the bromine. The bromine is not completely removed on reduction either with zinc dust and alcoholic hydrogen chloride or with aluminium amalgam. Bromination in acetic acid solution is accelerated in sunlight; it is a process of substitution. The product, bromodehydrocholic acid, crystallises from acetic acid or from acetone in needles, decomp. 180°; when crystallised from alcohol, it forms octahedra, decomp. ±140°.

Ethyl bromodehydrocholate is obtained either by brominating ethyl dehydrocholate or by esterification of bromodehydrocholic acid. The bromine is removed quantitatively by means of sodium hydroxide from either bromodehydrocholic acid or its ester. The bromo-acid is immediately oxidised by boiling Fehling's solution or ammoniacal silver solution. Zinc dust or magnesium reduce it to dehydrocholic acid.
E. F. A.

Preparation of the *p*-Bromophenylhydrazine Compound of Glycuronic Acid. ADOLF JOLLES (*Ber.*, 1912, **45**, 3280—3281).—In presence of traces of impurity the crystallisation of the *p*-bromophenylhydrazine compound of glycuronic acid is prevented (Neuberg, A., 1899, i, 933). After recrystallisation of the hydrazine, the lustrous, golden-yellow needles described by Neuberg are obtained without difficulty. E. F. A.

The Action of *p*-Bromophenylhydrazine on Glycuronolactone. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Monatsh.*, 1912, **33**, 1217—1231).—Attempts to prepare Neuberg's compound of *p*-bromophenylhydrazine with glycuronic acid (A., 1899, i, 933), which has also been prepared and analysed by Jolles (A., 1911, i, 709), have entirely failed either when Neuberg's original directions or modifications are followed. The products actually obtained were salts of *glycuronic acid* p-*bromophenylosazone*,
$CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C(N_2H\cdot C_6H_4Br)\cdot CH{:}N_2H\cdot C_6H_4Br$; *sodium* salt, hygroscopic, yellow needles, m. p. 185—190°, $[\alpha]_D$ (in alcohol and pyridine mixture) $-259°$; *barium* salt, hygroscopic, yellow

needles, m. p. 215—217° (decomp.); the *calcium, potassium, zinc*, and *lead* salts were also prepared.

It is suggested that the formation of the barium salt, which occurs easily and in good yield, constitutes a much more satisfactory test for glycuronic acid than does the evidently uncertain reaction of Neuberg.

D. F. T.

The Mechanism of Oxidation Processes. OSCAR LOEW (*Ber.*, 1912, 45, 3319).—When cuprous oxide is added to an alkaline solution of formaldehyde a vigorous evolution of hydrogen takes place, formic acid being formed. This experiment supports Wieland's idea (A., 1912, i, 944) that the oxidation of an aldehyde to an acid is a process of dehydrogenation.

T. S. P.

αα-Bromomethylpropaldehyde. II. The Friedel-Crafts Reaction. ADOLF FRANKE and ARTUR KLEIN (*Monatsh.*, 1912, 33, 1233—1241).—Polymeric αα-bromomethylpropaldehyde (monoclinic crystals, $a:b:c=2\cdot6:1:4\cdot9$; $\beta=90°7'$) only enters into synthetic reactions when the conditions are such as to cause depolymerisation (Franke, A., 1900, i, 206, 427). When treated with benzene, carbon disulphide, and aluminium chloride, hydrogen bromide is vigorously evolved and phenyl *iso*propyl ketone formed; the oxime, tablets, m. p. 75°, with acetic anhydride yielded an *acetate*, b. p. 147—149°/10 mm. Reduction of the ketone in aqueous alcohol by sodium amalgam gave phenyl*iso*propylcarbinol; *acetate*, b. p. 106—108°/9·5 mm.; the b. p. (222—224°) of the free carbinol was considerably lower than that given earlier (Claus and Sauer, A., 1892, i, 350). Finely divided silver or copper acts on the polymeric bromomethylpropaldehyde at 150° with the formation of *iso*butaldehyde, together with products of higher b. p.

D. F. T.

Catalytic Reactions at High Temperatures and Pressures. XXV. VLADIMIR N. IPATIEV (*Ber.*, 1912, 45, 3218—3226). In addition to reduction with hydrogen under pressure in the presence of reduced nickel as catalyst, the author investigates the action of reduced palladium as catalyst. In some cases the apparatus in which the reduction was being carried out was shaken at intervals only, whilst in other cases the contents were stirred continuously by means of a stirrer actuated by a solenoid.

Reduction of β-methyl-β-ethylacraldehyde takes place at 130° in the presence of reduced nickel, but the yield of alcohol is very small, a considerable quantity of condensation products being formed. With palladium as catalyst and a hydrogen pressure of 110 atmos., reduction takes place at 110° with the formation of γ-methyl-*n*-amyl alcohol, b. p. 145—146°/758 mm., D^{15} 0·8227. The reduction takes place slowly unless continuous stirring is resorted to. Attempts to reduce the above acraldehyde in the author's apparatus, using Skita's method (A., 1909, i, 479), were unsuccessful, either at the ordinary temperatures or at 100°.

With palladium as catalyst, mesityl oxide is slowly reduced at 100° to methyl *iso*butyl ketone, whereas with nickel as catalyst

mixture of methyl *iso*butyl ketone and methyl*iso*butylcarbinol is obtained at 145°.

The reduction of citral in the presence of palladium at 110°, or of a mixture of reduced nickel and nickel oxide at 140°, takes place slowly when the apparatus is continuously shaken. A mixture of products is obtained, from which $\beta\zeta$-dimethyloctane and $\gamma\eta$-dimethyloctanol were separated. When the reduction is carried out with continuous stirring, it proceeds rapidly to completion, the only product being decanol, b. p. 107—108°/12 mm., D^{18} 0·8296.

Under the same conditions as with citral, geraniol gives a mixture of decanol with small quantities of decane and condensation products when continuous shaking is resorted to, whereas with continuous stirring decanol and small quantities of decane are obtained.

At 109°, under a hydrogen pressure of 116 atmos., and in the presence of palladium as catalyst, acetylacetone is reduced to amylene $\beta\delta$-glycol, b. p. 197—198°, D^{18} 0·9602. With reduced nickel as catalyst, the reduction proceeds very slowly, the final product being a mixture of the original acetonylacetone with methyl *n*-propyl ketone.

By means of the apparatus with continuous stirring, the carbohydrates can readily be reduced; 20—30% aqueous-alcoholic solutions are used, the temperature being 110° with palladium as catalyst, and 130—135° with a mixture of reduced nickel and nickel oxide as catalyst; the hydrogen pressure is 100 atmos. With both catalysts, lævulose gives *d*-mannitol ($[\alpha]_D$ +0·71°), but the reduction is incomplete; dextrose is reduced to *d*-sorbitol ($[\alpha]_D$ +0·25°). Lactose is reduced to dulcitol. T. S. P.

The System Acetonephenylhydrazone-Water. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, 9, 924—927. Compare Reisenegger, A., 1883, 738; Schmidt, A., 1889, 1159; Arnold, A., 1897, i, 409).—The physical data for acetonephenylhydrazone given by the investigators named are incorrect. On heating acetone with a solution of phenylhydrazine in water or dilute acetic acid, an oil is formed. When it is washed with water, dried with potassium carbonate, and distilled under reduced pressure, the product is a pale yellow liquid, b. p. 116°/16 mm., 153°/31 mm., 160°/44 mm., 163°/50 mm. Repeated solidification by cooling with a freezing mixture yielded colourless crystals, m. p. 26·6°, which on exposure to air became yellow and then brown. It forms a colourless hydrate, turned brown, and ultimately resinified by the action of air.

The author gives the fusion curves of acetonephenylhydrazone, its hydrate, and water. The solubility of the hydrate per 100 c.c. of water is 0·09 gram (0°), 0·187 gram (15°), and 0·412 gram (32·8°).

A. J. W.

Syntheses by means of Mixed Organo-zinc Derivatives. α-Polychloroketones. Constitution of the Ordinary Trichloroacetone. EDMOND E. BLAISE (*Compt. rend.*, 1912, 155, 1252—1253. Compare A., 1912, i, 606).—Dichloroacetyl chloride readily condenses with α-hydroxy*iso*butyric acid to form *dichloroacetoxyisobutyric acid*, $CHCl_2\cdot CO_2\cdot CMe_2\cdot CO_2H$, m. p. 95°. The corresponding *acid chloride*,

b. p. 103°/12 mm., yields an *anilide*, m. p. 99—100°, and condenses with zinc ethyl iodide, giving the cyclo*acetal*, $C_8H_{12}O_3Cl_2$, m. p. ?°, b. p. 124·5—125°/16 mm., which on hydrolysis with a mixture of acetic and hydrochloric acids yields *dichloromethyl ethyl ketone*,

$CHCl_2·COEt$,

b. p. 138·5—139°. This ketone with hydroxylamine gives ethylglyoxaldioxime, m. p. 128°. Attempts to convert the ketone into the corresponding keto-aldehyde were not successful.

Trichloroacetoxyisobutyryl chloride, b. p. 113°/18 mm., can be similarly prepared, and gives an *anilide*, m. p. 100°. The *acid* has m. p. 117°, and with zinc methyl iodide gives the cyclo*acetal*,

$C_7H_9O_3Cl_3$,

m. p. 98—99°, which on hydrolysis yields *as*-trichloroacetone, $CCl_3·COMe$, b. p. 134°. Its *semicarbazone* crystallises in needles, m. p. 140°. Ordinary trichloroacetone, b. p. 172°, obtained by the chlorination of acetone, must therefore be the unsymmetrical compound (compare Schotterbeck, A., 1909, i, 553). W. G.

Action of Halogen Compounds of Phosphorus on Ketones, Bromo-ketones, and Keto-alcohols. ALEXEI E. FAVORSKI (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1339—1395).—According to Henry (*Ber.*, 1875, 8, 400) the action of phosphorus pentachloride on di*iso*propyl ketone results in replacement of the carbonylic oxygen by two atoms of chlorine, the compound thus formed giving βδ-dimethyl-$\Delta^{\beta\gamma}$-pentadiene when treated with alcoholic potassium hydroxide. The author finds, however, that the principal product of this action is not a dichloro-compound, but *iso*propyl α-chloro*iso*propyl ketone,

$CMe_2Cl·CO·CHMe_2$.

Further, in the case of *iso*propyl *tert.*-butyl ketone, the reaction proceeds similarly, α-chloro*iso*propyl *tert.*-butyl ketone being mainly obtained. With phosphorus pentabromide, the reaction takes place in the above direction with all ketones, and of a number of these compounds examined, only pinacolin underwent to some extent replacement of its carbonylic oxygen by two bromine atoms.

The ability of the carbonyl group of a ketone to react with phosphorus pentahaloid depends on the structure of the ketone and on its greater or less capacity to undergo enolisation. Ketones of normal structure (mono- and di-substituted acetones) readily react in the cold with phosphorus pentachloride by means of their carbonyl group, the oxygen of which is replaced by chlorine. On the other hand, such ketones as di*iso*propyl ketone, and, more especially *iso*propyl *tert.*-butyl ketone, react with phosphorus pentachloride only in the form when they undergo enolisation, the action of the chlorine liberated by dissociation of the pentachloride resulting in the formation of a monochloroketone:

(1) $CMe_2:O + PCl_5 = CMe_2Cl·OPCl_4 = POCl_3 + CH_3·CCl_2·CH_3$;

(2) $CHMe_2·CO·CHMe_2 \longrightarrow CMe_2:C(OH)·CHMe_2 + Cl_2 = CMe_2Cl·CO·CHMe_2 + HCl$.

Phosphorus pentabromide dissociates more readily, both on heating and in solution, than the pentachloride, and exerts, therefore, increased enolising action on the ketones, which yield mainly bromoketones.

$CMe:O \rightarrow CH_3 \cdot C(OH):CH_2 + Br_2 = CH_3 \cdot CO \cdot CH_2Br + HBr$. Experiment shows, indeed, that the action of bromine on ketones yields the same products as that of phosphorus pentabromide, the latter, however, acting more vigorously owing to the enolising action of the bromine formed on dissociation of the pentabromide being more energetic than the action of free bromine; for instance, *iso*propyl α-bromo*iso*propyl ketone is not acted on by bromine, but is converted into the dibromo-derivative when heated with phosphorus pentabromide on a water-bath.

The first bromine atom enters the ketone molecule in the α-position with respect to the carbonyl group and mostly replaces a hydrogen atom of the less highly hydrogenated hydrocarbon group. The second bromine atom proceeds mostly to the same carbon atom as the first, so that unsymmetrical αα-dibromoketones are obtained in preponderating amount. If, however, the first bromine atom replaces the only hydrogen atom combined with the first of the α-carbon atoms, the second bromine atom becomes united with the other carbon atom adjacent to the carbonyl group, symmetrical dibromoketones being obtained. Tribromoketones may also be formed by the replacement of all three hydrogen atoms united to the carbon atoms in the α-positions.

[With I. IDELSON and (Mlle.) A. UMNOVA.]—iso*Propyl α-chloro*iso*propyl ketone*, $CMe_2Cl \cdot CO \cdot CHMe_2$, is a colourless liquid, b. p. 142°/760 mm., 92°/150 mm., D_0^0 0·9800, D_0^{20} 0·9592, giving no compound with semicarbazide. By alcoholic potassium hydroxide it is converted into iso*butyryldimethylcarbinol*, $OH \cdot CMe_2 \cdot CO \cdot CHMe_2$, which is a colourless liquid with an odour like that of camphor, b. p. 164·5—165°/760 mm., D_0^0 0·9408, D_0^{20} 0·9239, and forms a *semicarbazone*, $C_8H_{17}O_2N_3$, m. p. 196°, in either aqueous or alcoholic solution (compare Kling, A., 1905, i, 503). Reduction of the keto-alcohol yields: (1) βγ-dihydroxy-βδ-dimethylpentane, $OH \cdot CMe_2 \cdot CHPr^{\beta} \cdot OH$, m. p. 59°, and (2) di*iso*propylcarbinol. Conversion of di*iso*propylcarbinol into the corresponding γ-iodo-βδ-dimethylpentane, $CHMe_2 \cdot CHI \cdot CHMe_2$, and treatment of the latter with alcoholic potassium hydroxide yields *βδ-dimethyl-Δ^β-amylene*, $CMe_2:CHPr^{\beta}$, b. p. 82—84°, oxidation of which gives *iso*butyryldimethylcarbinol (see above) (compare Blaise and Herman, A., 1910, i, 534).

[With E. FRICMAN.]—iso*Propyl* tert.-*butylcarbinol*,

$$OH \cdot CHPr^{\beta} \cdot CHMe_3,$$

obtained by the action of magnesium *tert*.-butyl chloride on *iso*butaldehyde, is a liquid, b. p. 150—151°/760 mm., D_0^0 0·8179, D_0^{20} 0·8298, m. p. −13°, with a camphor-like odour. On oxidation it yields iso*propyl* tert.-*butyl ketone*, $COPr^{\beta} \cdot CHMe_3$, which is a mobile liquid, b. p. 134—135°/760 mm., D_0^0 0·8240, D_0^0 0·8065, with an intense camphor-like odour; neither the hydrazone nor the semicarbazone could be obtained. Treatment of the ketone with phosphorus pentachloride in a sealed tube at 140° gives: (1) *α-chloro*iso*propyl* tert.-*butyl ketone*, $CMe_2Cl \cdot CO \cdot CMe_3$, b. p. 79—110°/18 mm., which yields Butlerov's acetenol, $\overset{CMe_2}{\underset{O}{|}}\!\!>C(OH) \cdot CMe_3$ (A., 1882, 936), on treatment with

potassium hydroxide solution; (2) *γγ-dichloro-ββδ-trimethylpentane*
$CMe_3\cdot CCl_2\cdot CHMe_2$,
b. p. 122—125°/19 mm.

[With B. Isatschenko.]—The action of phosphorus pentabromide on acetone yields bromoacetone, and that of the pentabromide or bromine (1 mol.) on methyl ethyl ketone gives *methyl α-bromoethyl ketone*, which is a liquid, b. p. 35—38°/12 mm., D_{20}^{20} 1·4380. With 2 mols. of bromine, methyl ethyl ketone yields (1) *bromomethyl α-bromoethyl ketone*, $CH_2Br\cdot CO\cdot CHMeBr$, b. p. 194—195°, 80—85°/10 mm., D_{20}^{20} 1·9729; (2) a tribromo-derivative of the ketone.

[With A. Vanscheidt.]—The action of phosphorus pentabromide on methyl *iso*propyl ketone yields: (1) *Methyl α-bromo*iso*propyl ketone*, $CH_3\cdot CO\cdot CMe_2Br$, b. p. 49°/22 mm., 139°/760 mm., D_4^{20} 1·3377, which is converted into acetyldimethylcarbinol (compare Diels and Johlin, A., 1911, i, 254) when heated in a sealed tube with potassium formate at 130° (compare Kling, A., 1905, i, 503); the *acetyl* derivative of the carbinol, $C_7H_{12}O_3$, b. p. 65°/15 mm., 170—171°/760 mm., forms the *oxime*, $C_7H_{13}O_3N$, m. p. 102—103°. (2) *Bromomethyl α-bromo*iso*propyl ketone*, $CH_2Br\cdot CO\cdot CMe_2Br$, which is best obtained by the action of bromine on the preceding compound, and is a colourless liquid, b. p. 99°/18 mm., m. p. 10°, D_{20}^{20} 1·830, yielding no crystalline products with hydroxylamine, phenylhydrazine, or semicarbazide. With alcoholic potassium hydroxide (compare Favorski, A., 1895, i, 496; Semenov, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 693) it yields ββ-dimethylacrylic acid (compare Weinig, A., 1895, i, 17). (3) *Dibromomethyl α-bromo*iso*propyl ketone*, $CHBr_2\cdot CO\cdot CMe_2Br$, which forms colourless, silky needles, m. p. 52°, b. p. 110—115°/6 mm., D_{21}^{52} 2·051, D_{21}^{21} 2·268. By aqueous potassium hydroxide, this ketone is converted into ββ-dimethylglyceric acid, $OH\cdot CMe_2\cdot CH(OH)\cdot CO_2H$, the *iso*butyl ester of which, $C_9H_{18}O_4$, is a viscous liquid, b. p. 230° (decomp.), 121°/11 mm., D_{21}^{21} 1·0774, D_4^{21} 1·0752. When distilled in presence of sulphuric acid, ββ-dimethylglyceric acid yields α-hydroxy*iso*butaldehyde. These three bromo-ketones are also obtainable from methyl *iso*propyl ketone by the action of bromine, which gives, in addition, a *tetrabromo*-derivative, $C_5H_6OBr_4$, b. p. 157°/27 mm., D_{21}^{21} 2·446.

[With T. Velitschkovski.]—The action of phosphorus pentabromide on pinacolin yields: (1) *Bromomethyl* tert.-*butyl ketone*, $CH_2Br\cdot CO\cdot CMe_3$, which is a liquid with a pungent odour, b. p. 70—73°/9 mm., D_0^{20} 1·3274, D_0^0 1·3508, and reduces Fehling's solution in the cold. When heated with water and freshly-precipitated barium carbonate, it yields *hydroxymethyl* tert.-*butyl ketone*, $OH\cdot CH_2\cdot CO\cdot CMe_3$, which is a liquid, b. p. 158—160°, 52·5°/12 mm., m. p. +9·5°, D_{20}^{20} 0·95295, D_0^{20} 0·95164, $D_0^{13·5}$ 0·9576, and yields an *oxime*, $C_6H_{13}O_2N$, m. p. 89—90°, and a *phenylosazone*, $C_{18}H_{22}N_4$, m. p. 119—120°. Oxidation of this keto-alcohol yields first the corresponding keto-aldehyde and then α-hydroxy-ββ-dimethylbutyric acid, $CO_2H\cdot CH(OH)\cdot CMe_3$. (2) Dibromomethyl *tert.*-butyl ketone, $CHBr_2\cdot CO\cdot CMe_3$ (compare Kondakov, A., 1899, i, 859; Wittorf, A., 1900, i, 421). (3) *ββ-Dibromo-γγ-dimethylbutane*, $CH_3\cdot CBr_2\cdot CMe_3$, m. p. 191—191·5°.

[With D. SCIBORSKI.]—The action of phosphorus pentabromide on ethyl *iso*propyl ketone yields: (1) *Ethyl* α-*bromoisopropyl ketone*, $CBrMe_2·COEt$, b. p. 50—53°/13 mm., D_4^{20} 1·2847, D_4^0 1·3098, which gives *ethyl* α-*hydroxy*iso*propyl ketone*, $OH·CMe_2·COEt$, b. p. 95—97°/760 mm., D_4^0 0·9548, D_4^{20} 0·9446, D_{20}^{20} 0·9405, when heated with water and freshly-precipitated barium carbonate, and (2) α-*bromoethyl* α-*bromoisopropyl ketone*, $CHMeBr·CO·CMe_2Br$, b. p. 80—81°/13 mm.

[With P. ASCHMARIN.]—*Ethyl*tert.-*butylcarbinol*, $OH·CHEt·CMe_3$, obtained by the interaction of magnesium *tert.*-butyl chloride and propaldehyde, is a liquid, b. p. 132—135°, 42—44°/15 mm., D_4^0 0·84078, D_4^{20} 0·82462. It forms an *acetyl* derivative, $C_9H_{18}O_2$, b. p. 157—159°/770 mm., and on oxidation yields *ethyl* tert.-*butyl ketone*, $CMe_3·COEt$, b. p. 125—126°/769 mm., D_4^0 0·8303, D_4^{20} 0·8125, which gives a *semicarbazone*, $C_8H_{17}ON_3$, m. p. 144°. The action of phosphorus pentabromide on this ketone yields: (1) α-*Bromoethyl* tert.-*butyl ketone*, $CHMeBr·CO·CMe_3$, b. p. 67·5—68·5°/11 mm., D_4^0 1·2687, D_4^{20} 1·2456, and (2) αα-*dibromoethyl* tert.-*butyl ketone*, $CMeBr_2·CO·CMe_3$, m. p. 77·5—79°/10 mm., D_4^0 1·5955, D_4^{20} 1·5674. *Trimethylacetylmethylcarbinol*, $OH·CHMe·CO·CMe_3$, obtained by way of its *acetyl* derivative, $OAc·CHMe·CO·CMe_3$, b. p. 189—191°, from α-bromoethyl *tert.*-butyl ketone, is a liquid, b. p. 100—101·5°/100 mm., D_4^0 0·9483, D_4^{20} 0·9301, with a faint camphor-like odour and yields a *semicarbazone* in two modifications, m. p. 98—100° and 135° respectively.

[With (Mlle.) A. UMNOVA.]—The action of bromine on di*iso*propyl ketone yields iso*propyl* α-*bromoisopropyl ketone*, $CMe_2Br·CO·CHMe_2$, b. p. 166—168°, 50—51°/10 mm., D_0^0 1·2763, D_0^{20} 1·2636, which is converted by phosphorus pentabromide into *di*-α-*bromoisopropyl ketone*, $CO(CMe_2Br)_2$, a yellow liquid with an odour of camphor, b. p. 84—85°/9 mm., D_0^0 1·6441, D_0^{20} 1·6174. *Di*-α-*hydroxyisopropyl ketone*, $CO(CMe_2·OH)_2$, obtained by the action of aqueous potassium hydroxide on the dibromo-ketone, forms rhombic plates, m. p. 42—43°, b. p. 101·5—102°/11 mm., gives a *diacetyl* derivative, $C_{11}H_{18}O_5$, m. p. 51—52°, and is converted by magnesium methyl iodide and water into *pentamethylglycerol*,

$$OH·CMe_2·CMe(OH)·CMe_2·OH,$$

which crystallises in slender, shining needles or prisms, m. p. 118—119°. When heated with 2% sulphuric acid solution, the trihydric alcohol decomposes into acetone and methyl *iso*propyl ketone.

[With G. BRILIANT.]—The action of phosphorus pentabromide on *iso*propyl *tert.*-butyl ketone yields α-*bromoisopropyl* tert.-*butyl ketone*, $CMe_3·CO·CMe_2Br$, b. p. 91—93°/40 mm., 62—64°/12 mm., D_0^0 1·2441, D_0^{20} 1·2233, which gives a good yield of Butlerov's oxoctenol (see above) when heated with 10% aqueous potassium hydroxide.

[With (Mlle.) A. ZACHAROVA.]—iso*Propyl*iso*butylcarbinol*,

$$CHMe_2·CH(OH)·CH_2·CHMe_2,$$

obtained by the action of magnesium *iso*butyl bromide on *iso*butaldehyde, has b. p. 156°, D_0^0 0·8325, D_0^{20} 0·8222, and on oxidation yields iso*propyl* iso*butyl ketone*, $CHMe_2·CO·CH_2·CHMe_2$, b. p. 147—148°, D_0^0 0·82705, D_0^{20} 0·81223. α-*Bromo*iso*propyl* iso*butyl ketone*, $CMe_2Br·CO·CH_2·CHMe_2$, obtained by the action of either bromine or

phosphorus pentabromide, has b. p. 75—78°/12 mm., 81—85°/21 mm., D_0^0 1·2187, D_0^{20} 1·1979, and, when heated with potassium formate and methyl alcohol in a sealed tube at 120°, yields *isobutyryldimethylcarbinol*, $OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CHMe_2$, b. p. 67—70°/13 mm., D_0^0 0·915, D_0^{20} 0·8962, the *semicarbazone* of which, $C_9H_{19}O_2N_3$, m. p. 126°, was prepared; oxidation of the keto-alcohol gives valeric acid. α-*Bromoisopropyl α-bromoisobutyl ketone*, $CMe_2Br\cdot CO\cdot CHBr\cdot CHMe_2$, b. p. 103—105°/21 mm., is also formed by the action of phosphorus pentabromide on *iso*propyl *iso*butyl ketone.

[With N. Mandryk.]—*Phenylisopropylcarbinol*, $OH\cdot CHPh\cdot CHMe_2$, prepared by the action of magnesium *iso*propyl iodide on benzaldehyde, has b. p. 110—111°/13 mm., D_0^0 0·9933, D_{20}^{20} 0·9790, forms the *acetyl* derivative, $C_{12}H_{16}O_2$, b. p. 118—120°/16 mm., and on oxidation yields *phenyl isopropyl ketone*, $CHMe_2\cdot COPh$, which is a colourless liquid, b. p. 95—98°/10 mm., D_0^0 0·9996, D_{20}^{20} 0·9848, and forms the *semicarbazone*, $C_{11}H_{15}ON_3$, m. p. 166—167°. The action of phosphorus pentabromide on the ketone yields phenyl α-bromo*iso*propyl ketone, b. p. 129—130°/12 mm., D_0^0 1·3845, D_{20}^{20} 1·3652 (compare Collet, A., 1898, i, 477). *Benzoyldimethylcarbinol*, $CMe_2Bz\cdot OH$, b. p. 116—118°/9 mm., D_0^0 1·0928, D_{20}^{20} 1·0775, when kept in a sealed tube for some months, forms the *compound*, $CMe_2Bz\cdot O\cdot CMe_2Bz$ or

$$\begin{matrix} O \text{——} \\ | \\ CMe_2 \end{matrix}\!\!>CPh\cdot O\cdot CPh<\!\!\begin{matrix} O \\ | \\ CMe_2 \end{matrix},$$

m. p. 185—186°.

[With (Mlle.) L. Kolotova.]—The action of phosphorus pentabromide on *cyclo*hexyl methyl ketone yields *bromocyclohexyl methyl ketone*, $CBrAc<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$, b. p. 97—101°/13 mm., and this, with heated with aqueous potassium hydroxide, gives 1-*acetylcyclohexan-1-ol*, $C_6H_{10}Ac\cdot OH$, b. p. 92—94°/18 mm., D_0^0 1·0125, D_0^{20} 1·02569, which forms the *semicarbazone*, $C_9H_{17}O_2N_3$, m. p. 102° (decomp.), but does not yield a phenylosazone or react with Fehling's solution. On oxidation, 1-acetyl*cyclo*hexan-1-ol yields *cyclo*hexanone and acetic acid.

[With M. Charitonova.]—The action of phosphorus pentabromide on *cyclohexyl isopropyl ketone*, $C_6H_{11}\cdot CO\cdot CHMe_2$, b. p. 83°/11 mm., which was prepared from magnesium *cyclo*hexyl bromide and *iso*butaldehyde, yields *cyclohexyl α-bromoisopropyl ketone*, $C_6H_{11}\cdot CO\cdot CMe_2Br$, b. p. 111—112°/10 mm., m. p. 29°. On oxidation, the latter gives *cyclohexyl α-hydroxyisopropyl ketone*, $C_6H_{11}\cdot CO\cdot CMe_2\cdot OH$, b. p. 97—98°/11 mm., D_0^0 0·9764, D_0^{20} 0·9655, the *semicarbazide* of which, $C_{11}H_{21}O_2N_3$, m. p. 183°, was prepared. Oxidation of the keto-alcohol yields hexahydrobenzoic and acetic acids. T. H. P.

Sugar Solutions and Calcium Hydroxide. P. J. H. van Ginneken (*Zeitsch. ver. deut. Zuckerind*, 1912, 1293—1295).—Polemical. A reply to the criticisms of Weisberg (A., 1912, i, 608). E. F. A.

Photolysis of Sucrose by Ultra-violet Rays. Daniel Berthelot and Henri Gaudechon (*Compt. rend.*, 1912, **155**, 1016—1018. Compare A., 1910, ii, 813, 814; 1912, i, 750).—Working with rays (λ = 0·25μ)

the photolysis of sucrose can be shown to take place in two stages, the first, lasting six hours and consisting of hydrolysis of the sucrose to dextrose and lævulose, the solution remaining neutral, and no gas being evolved; and the second, of the decomposition of these two hexoses with the evolution of carbon monoxide and hydrogen, the relative volumes of these gases liberated pointing to the more rapid decomposition of the lævulose than the dextrose. With the extreme ultra-violet rays the first stage is very rapid, and the separation of the two phases is somewhat difficult. W. G.

Composition of Press Cakes from Sugar Refineries. LÉON LINDET and CHARPENTIER (*Bull. Soc. chim.*, 1912, [iv], 11, 956—958).—It is shown that these cakes, after having been properly washed by the slightly ammoniacal water produced by condensing steam from the evaporating pans, contain no free lime. The sugar, which can be extracted by washing them with water, is present in the free state. The cakes always contain insoluble tribasic calcium saccharate, owing to the fact that this compound is not decomposed in the customary rapid treatment with carbon dioxide. T. A. H.

Plant Colloids. II. The Stability of Starch Solutions. MAX SAMEC (*Koll. Chem. Beihefte*, 1912, 4, 132—174. Compare A., 1912, ii, 141).—The ageing of starch solutions is accompanied by a very considerable reduction of the viscosity, and the influence of foreign substances on the changes which occur during the process of ageing has been investigated by means of viscosity measurements. The same starch was used for all the experiments, and the solutions prepared by mixing a weighed quantity of the starch to a paste with 25 c.c. of cold water and then adding the paste to 75 c.c. of boiling water. After boiling for one minute, the starch paste was heated for two hours at 120° and then filtered under pressure, the age of the starch solution being reckoned from the time of the completed filtration.

The rate of diminution of the viscosity of such starch solutions is greater for dilute than for more concentrated solutions. It is also greater for solutions which have been shaken than for corresponding solutions which have been kept undisturbed. The addition of hydrochloric acid diminishes the initial viscosity, but retards the further progress of the change, and thus increases the stability of the solutions. With increasing concentration of the acid, the influence on the stability increases at first and passes through a maximum. Potassium hydroxide raises the viscosity when added in very small quantity; if larger amounts are present the viscosity is diminished, however, and this effect is very pronounced in the case of solutions which contain alkali hydroxide in more than $0·001N$-concentration. Ammonium sulphate and ammonium thiocyanate both diminish the initial viscosity, but in concentrated solution the influence of the two salts on the stability of the starch solution is quite different, in that the sulphate increases the stability, whilst the thiocyanate is comparatively inactive.

The viscosity change is irreversible in character, and the sensitiveness of the starch solutions towards electrolytes diminishes with the time which has elapsed since their preparation. The ageing of the

solutions is also found to be accompanied by an increase in the electrical conductivity.

An explanation of some of the observed facts is suggested, in which the author assumes that the active constituent is a complex compound of starch and phosphoric acid. H. M. D.

Photochemical Synthesis of Carbohydrates. Julius Stoklasa, Johann Šebor, and Wenzel Zdobnický (*Biochem. Zeitsch.*, 1912, 47, 186—188. Compare A., 1912, i, 606).—A reply to the criticisms of Walther Löb (A., 1912, i, 750). S. B. S.

Existence of a Hydrate of Nitrocellulose. Th. Chandelon (*Bull. Soc. chim. Belg.*, 1912, 26, 495—502).—The viscosities of solutions of dry and moist nitrocelluloses in mixtures of alcohol and ether have been examined, together with the viscosities of solutions of dry nitrocellulose in the same mixture to which small quantities of water have been added.

The author is led to the conclusions: (1) that the greater solubility of moist nitrocellulose in a mixture of alcohol and ether does not depend on the existence of a hydrate, but simply on the dilution of the solvent by the water contained in the moist substance; (2) that it is immaterial whether this water is contained in the moist nitrocellulose or previously added to the solvent, and (3) that a mixture of alcohol and ether which contains small quantities of water has a solvent action towards nitrocellulose superior to that of an anhydrous mixture of the two solvents. H. W.

A New Nitrocellulose. Tassart (*Bull. Soc. chim.*, 1912, [iv], 11, 1009—1011).—By the successive action of sulphuric acid and nitric acid on cotton with avoidance of rise in temperature, the author has obtained a white, powdery unstable compound which is provisionally termed α-nitrocellulose and which contains about 13·5% nitrogen. When heated on the water-bath it becomes pasty, evolves nitrous fumes with increasing intensity, and ultimately ignites. In thin layers, however, heating can be conducted without inflammation, when the residue, after cessation of evolution of nitrous fumes, is found to contain 6% nitrogen and to reduce Fehling's solution. The latter property is not possessed by α-nitrocellulose to any marked extent.

Certain substances, such as diphenylamine, dextrose, diaminophenol hydrochloride, α-naphthylamine, tetramethyldiaminobenzophenone, etc., when warmed with α-nitrocellulose on the water-bath cause darkening and subsequent charring without evolution of nitrous fumes or inflammation. On the other hand, the tendency of α-nitrocellulose towards spontaneous inflammability is accentuated by the presence of *p*-phenylenediamine.

α-Nitrocellulose is insoluble in water, soluble in methyl and ethyl alcohols, aldehyde, and acetone. Treatment with water or aqueous sodium hydroxide leaves it unaffected, but alcoholic sodium hydroxide causes marked alteration in properties, and renders it completely soluble in water.

Dextrose and amidon, when similarly treated with sulphuric and nitric acids, yield similar products. H. W.

Formylated Cellulose. EDWARD C. WORDEN (*J. Soc. Chem. Ind.*, 1912, **31**, 1064—1068).—The author discusses at some length the several methods of preparing cellulose acetates and formates which have been published, also the means which have been devised for converting these esters into plastic substances resembling celluloid.

Results of work carried out with the object of converting cellulose formate, obtained by the action of formic acid (99%) and zinc chloride on a cellulose prepared by denitrating nitro-cellulose with ammonium sulphide solution, into a modification having more valuable properties, such as greater solubility in common organic solvents, are recorded.

The crude solutions of cellulose formate as obtained directly from the cellulose were treated with small quantities of water for varying periods. Generally speaking, the effect of this treatment is to increase the solubility of the product in solvents such as acetone, chloroform, and tetrachloroethane, the solubility becoming greater as the proportion of water employed or the period of treatment is increased. W. H. G.

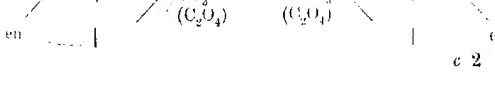
Neurine Bromide. ERNST SCHMIDT and A. SEEBERG (*Apoth. Zeit.*, 1912, **71**; Reprint, 2 pp.).—The conversion of large quantities of trimethylbromoethylammonium bromide into neurine by moist silver oxide is often accompanied by serious loss, due to the formation of trimethylamine. A cheaper and more satisfactory method is described, in which barium hydroxide is used in place of silver oxide.

Neurine bromide on heating with hydrobromic acid at 165—170° gives, as already observed, trimethyl-β-bromoethylammonium bromide, but the mother liquors contain another substance, apparently the isomeric *trimethyl-α-bromoethylammonium bromide*, crystallising in tablets. D. F. T.

The Asymmetric Cobalt Atom. VI. ALFRED WERNER and MCCUTCHEON (*Ber.*, 1912, **45**, 3281—3287).—The active compounds of cobalt which have hitherto been prepared belonging to the series $[en_2CoX_2]X$ contain two monobasic acid residues in direct combination with the cobalt atom, for example, $[Cl_2Co\,en_2]X$ and $[(NO_2)_2Co\,en_2]X$. The authors have now investigated the compounds in which the two X-groups have been replaced by one dibasic acid residue, for example, the oxalic and carbonic acid residues, in order to see if they show mirror-image isomerism. These compounds have the following structural formulæ: $\left[\begin{matrix}O{:}C{\cdot}O \\ | \\ O{:}C{\cdot}O\end{matrix}\!\!>\!Co\,en_2\right]X$ and

$$\left[O{:}C\!<\!\begin{matrix}O\\O\end{matrix}\!>\!Co\,en_2\right]X.$$

It has been shown previously (A., 1912, i, 78) that geometrical isomerides do not exist, and that the acid residues occupy neighbouring co-ordination positions. Optical isomerides should, however, exist in accordance with the following scheme:



It was not found possible to resolve the inactive compounds into their active components, but the individual isomerides have been obtained directly from the active 1:2-dichlorodiethylenediaminecobaltic salts by the action of potassium carbonate and oxalate respectively, for example: $[Cl_2Co\,en_2]Cl + K_2CO_3 = [CO_3Co\,en_2]Cl + 2KCl$. The fact that such active isomerides have been prepared forms further support for the *cis*-structure of these compounds.

The active carbonato-salts possess an intense red colour, so that their rotatory power could only be determined for red light (*C* line). The observed specific rotations are fairly large, for example, the chloride has $[\alpha]_c \pm 350°$, and it is noteworthy that the various salts show very different rotatory powers, the iodide having $[\alpha]_c \pm 250°$ and the dithionate $[\alpha]_c \pm 216°$. In cold aqueous solution the salts are fairly stable, undergoing racemisation very slowly, the rotation diminishing by one-half in about eight days. At 90° racemisation is complete in a short time. The products of racemisation consist of the inactive carbonato-salts, and are formed probably by one of the valencies of the carbonato-residue becoming loosened for a time, the radicle [Co en₂ then undergoing a structural change.

The oxalo-salts possess a smaller specific rotation than the carbonato-salts, the chloride and nitrate having $[\alpha]_c \pm 200°$ and the iodide $[\alpha]_c \pm 160°$. They are quite stable, the aqueous solutions showing no tendency to racemise even on warming.

The sign of rotation of the various carbonato- and oxalo-salts is the opposite to that of the dichloro-salts from which they are obtained.

Carbonato-salts, YX, where $Y = [CO_3Co\,en_2]$.—The d- and l-*chlorides*, YCl, are obtained by heating a mixture of 1 gram of the active dichloro-chloride with the calculated quantity of potassium carbonate and 0·5 c.c. of water on the water-bath until the colour changes to red (2 mins.). The reaction product is then rapidly cooled in a freezing mixture and rubbed with a platinum spatula, when the chloride separates as a red, crystalline powder, forming a mixture of the active and racemic compounds. The racemate is less soluble than the active salt, and is left undissolved when sufficient water is added to dissolve about three-quarters of the solid. The pure active chloride is then obtained from the aqueous solution by precipitation with a mixture of alcohol and ether. $[\alpha]_c \pm 350°$, $[M]_c \pm 960°$; 100 c.c. of water dissolve 5 grams of the active chloride at 18°.

The active *iodides*, YI, and *dithionates*, $Y_2S_2O_6$, were obtained from the active chlorides by double decomposition with ammonium iodide and sodium dithionate respectively. The former have $[\alpha]_c \pm 250°$, $[M]_c \pm 915°$, and dissolve to the extent of 1 gram in 100 c.c. of water at 18°; the latter has $[\alpha]_c + 216°$ and $-220°$, $[M]_c + 689°$ and $-702°$, the solubility being 3·5 grams of the salt in 100 c.c. of water at 18°.

Oxalo-salts, YX, where $Y = [C_2O_4Co\,en_2]$.—The active *chlorides*, YCl,H_2O, are prepared similarly to the carbonato-salts, using potassium oxalate, the chief difference being that the racemate is more soluble than the active salt, the latter separating out fairly pure. $[\alpha]_c + 200°$ and $-204°$, $[M]_c + 641°$ and $-653°$; 100 c.c. of water

dissolve 2 grams of the salt at 18°. The active *iodides*, YI, and *nitrates*, YNO_3,H_2O, were obtained from the chloride by double decomposition with ammonium iodide and silver nitrate respectively. Their solubilities are respectively 1 gram and 4 grams in 100 c.c. of water at 18°. The former have $[\alpha]_c + 160°$ and $-155°$, $[M]_c + 630°$ and $-610°$, the latter having $[\alpha]_c + 204°$ and $-200°$, $[M]_c + 689°$ and $-676°$.

T. S. P.

The Asymmetric Cobalt Atom. VII. ALFRED WERNER and YUJI SHIBATA (*Ber.*, 1912, **45**, 3287—3293).—Optically active 1 : 2-diamminediethylenediaminecobaltic salts have now been obtained. They could not be prepared by resolution of the racemates, but were obtained from the active 1 : 2-bromoammine salts by the action of liquid ammonia, in accordance with the equation: $\left[\begin{matrix}Br\\NH_3\end{matrix}Co\,en_2\right]X_2 + NH_3 = \left[\begin{matrix}NH_3\\NH_3\end{matrix}Co\,en_2\right]\begin{matrix}X_2\\Br\end{matrix}$. This reaction denotes a change from an asymmetric cobalt compound to one showing molecular asymmetry I (compare A., 1911, i, 839).

1 : 2-Bromoamminediethylenediaminecobaltic bromide was used in the first experiments, but it was found that the active 1 : 2-diammine bromide obtained was always contaminated with the inactive 1 : 6-salt. The formation of the 1 : 6-isomeride was completely prevented, however, when the bromocamphorsulphonate was used instead of the bromide Recrystallisation of the product of the action of liquid ammonia on 1 : 2-bromoamminediethylenediaminecobaltic *d*-bromocamphorsulphonate gives immediately pure d-*diamminediethylenediaminecobaltic* d-*bromocamphorsulphonate*.

The active salts show very marked dispersion of the rotation, for example, the chloride has $[\alpha]_c \pm 15°$, $[\alpha]_D \pm 50°$; in the three-field polarimeter the *d*-salts give a yellow middle field and orange outer fields, the colours being reversed for the *l*-salts. Their rotatory powers for the *D*-line agree approximately with those of the dinitro-salts, and are about one-third of the values obtained for the triethylenediamine salts for both the *C*- and *D*-lines.

The solubilities of the active salts are, as a rule, greater than that of the racemate. Of the bromocamphorsulphonates, the *dd*- and *ll*-salts are sparingly soluble, whilst the *dl*- and *ld*-salts are easily soluble.

The cold aqueous solutions of the active salts can be preserved indefinitely without undergoing racemisation; on boiling for some time, racemisation occurs, being accompanied by a complete decomposition of the compounds.

d-*Diamminediethylenediaminecobaltic* d-*bromocamphorsulphonate* and the corresponding ll-*salt* were obtained by dissolving *d*-bromoamminediethylenediaminecobaltic *d*-bromocamphorsulphonate or the corresponding *ll*-salt in liquid ammonia. After a short time the solution turns yellow, and one recrystallisation of the residue after allowing the ammonia to evaporate gives the pure salt, $[\alpha]_D^{24} + 81°$ and $-80°$.

The following active diamminediethylenediaminecobaltic salts, YX_3,

where $Y=[(NH_3)_2Co\ en_2]$, were obtained from the active bromocamphorsulphonates by treatment with concentrated solutions of the appropriate acids. The *chlorides*, YCl_3, form golden-yellow prisms; the *bromides*, YBr_3, crystallise in deep-yellow needles; the *perchlorates*, $Y(ClO_4)_3$, form yellow, prismatic crystals, and the *nitrates*, $Y(NO_3)_3$, give slender, golden-yellow, flat crystals. The *iodides*, YI_3, dark yellow crystals, and the *dithionates*, $Y(S_2O_6)_3,3{\cdot}5H_2O$, small, cubical crystals, are obtained from the bromides by double decomposition with ammonium iodide and sodium dithionate respectively; the nitrate can similarly be obtained, using silver nitrate.

The specific and molecular rotations of the various salts are shown in the following table:

	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_C$.	$[M]_C$.	Temp.
d-Chloride	+50°	+159·8°	+15°	+47·94°	21·5
l-Chloride	−51	−162·99	−16	−51·14	22·0
d-Bromide	+37	+164·0	+11	+48·75	23·0
l-Bromide	−37	−164·0	−9	−39·89	22·0
d-Iodide	+29	+172·3	—	—	21·0
l-Iodide	−28	−166·22	—	—	24·0
d-Nitrate	+46	+183·7	+14	+55·89	21·5
l-Nitrate	−44	−175·65	−12	−47·90	23·5
d-Perchlorate	+32	+163·7	—	—	22·6
l-Perchlorate	−33	−168·83	−7	−35·81	22·0
d-Dithionate	+24	+116·86	—	—	23·0

T. S. P.

The Asymmetric Cobalt Atom. VIII. ALFRED WERNER and G. TSCHERNOV (*Ber.*, 1912, **45**, 3294—3301).—Optically active 1:2-chlorobromodiethylenediaminecobaltic salts, $\left[\begin{smallmatrix}Cl\\Br\end{smallmatrix}Co\ en_2\right]X$, are described. The inactive 1:2-chlorobromo-bromide, which was used as the starting point, was obtained as follows: 1:6-dichlorodiethylenediaminecobaltic chloride (compare A., 1912, i, 82) was prepared, and transformed into 1:2-chloroaquodiethylenediaminecobaltic sulphate. From the latter, chloroaquodiethylenediaminecobaltic bromide was obtained and transformed, by heating at 105°, into a mixture of the 1:2- and 1:6-chlorobromodiethylenediaminecobaltic bromide, from which the 1:2-isomeride is obtained by means of its lesser solubility (compare A., 1912, i, 83).

The active chlorobromo-salts were obtained by treating an aqueous solution of the racemic bromide with active ammonium bromocamphorsulphonate (compare the preparation of the active dichloro-salts, A., 1912, i, 11). After a short time, when ammonium *d*-bromocamphorsulphonate is used, a microcrystalline precipitate of *l*-chlorobromodiethylenediaminecobaltic *d*-bromocamphorsulphonate separates, whereas ammonium *l*-bromocamphorsulphonate gives the *dl*-salt. The salts are very unstable in aqueous solution, readily giving the bromoaquo-salts, so that all operations must be carried out as quickly as possible.

The various active salts were obtained from the bromocamphorsulphonates by trituration with the requisite concentrated mineral acid until complete solution was attained; the strongly-cooled solutions were then precipitated with alcohol.

The following table (rows 1 and 2) gives a summary of the rotatory powers of the various salts; for the sake of comparison, the rotations of the dichloro-salts are also given (rows 3 and 4):

	Chloride.		Bromide.		Nitrate.		Sulphate.		Dithionate.	
	[α].	[M].	[α].	[M].	[α].	[M].	[α].	[M]/2.	[α].	[M]/2.
d-Salt...	+164°	+571°	+148°	+581°	+144°	+513°	+144°	+506°	+116°	+445°
l-Salt...	−176	−612	−155	−608	−152	−542	−148°	−520	120	−460
d-Salt...	+184	+558	+168	+554	+164	+511	+180	+536	+160	+542
l-Salt...	−200	−607	−176	−581	−164	−511	−182	−540·5	−164	−556

The above are the maximum values observed, since racemisation takes place very rapidly.

l-*Chlorobromodiethylenediaminecobaltic* d-*bromocamphorsulphonate*,

$$Y(SO_3 \cdot C_{10}H_{14}OBr),$$

where $Y = \left[\begin{matrix} Cl \\ Br \end{matrix} Co\,en_2\right]$, forms a grey, crystalline powder with a violet shade; $[\alpha]^{20} - 40°$, $[M]^{20} - 242°$. The corresponding dl-*salt* is similar; $[\alpha]^{20} + 32°$, $[M]^{20} + 193°$. The active *chlorobromodiethylenediaminecobaltic chlorides*, YCl,H_2O, are dark, greyish violet, crystalline powders, as also are the *bromides*, YBr,H_2O, and the *nitrates*, YNO_3. The *sulphates*, Y_2SO_4,H_2O, and *dithionates*, $Y_2S_2O_6,H_2O$, are respectively light violet, crystalline powders and light grey leaflets.

T. S. P.

α-Aminobutyric Acid and its Derivatives. EMIL ABDERHALDEN and ERICH WURM (*Zeitsch. physiol. Chem.*, 1912, 82, 167—171. Compare Abderhalden and Chang, A., 1912, i, 338).—When pure α-aminobutyric acid is treated with concentrated hydrochloric acid under the conditions prevailing during protein hydrolysis, only about 5% of the acid undergoes decomposition. Alanine and leucine remain unchanged under these conditions.

The conditions for the preparation of pure formyl-*d*- and -*l*-aminobutyric acid are described. Formyl-*d*-aminobutyric acid has $[\alpha]_D^{20} - 27·74°$, the value for the isomeride being $+27·98°$.

The formyl group is readily hydrolysed by water.

On feeding *dl*-aminobutyric acid or glycyl-*dl*-aminobutyric acid to rabbits, neither the acids nor their components could be detected in the urine.

E. F. A.

Preparation of Creatine from Urine. ALOIS VIQUERAT (D.R.-P. 251937).—A modification of Neubauer's method (compare Abderhalden, *Lehrbuch Biochem. Arbeitsmethoden*, 1910, III, 783) by which creatine is isolated from urine as its zinc chloride double salt.

F. M. G. M.

Some Complex Compounds of Platinous Chloride with Aminoacetal. J. TSCHUGAEV and B. ORELKINE (*Compt. rend.*, 1912, 155, 1021—1023).—An endeavour to prepare two isomeric substances of the type, $[Pt(NHMe_2)_2Cl_2]$, prepared by Jörgensen (A., 1906, i, 338), replacing the dimethylamine by aminoacetal. On adding aminoacetal to a dilute solution of potassium platinosochloride, a yellow, crystalline compound is deposited, crystallising from alcohol in needles,

m. p. 133°. It has the composition ($Pt2ACl_2$), where A stands for the aminoacetal molecule, $NH_2\cdot CH_2\cdot CH(OEt)_2$. This substance is a very feeble electrolyte, and is almost unacted on by silver nitrate in alcoholic solution. In benzene solution it polymerises as shown by cryoscopic molecular weight determinations. The mother liquors from its preparation on evaporation yield a colourless, crystalline *compound*, ($Pt4A)Cl_2$, m. p. 130·5°, the chlorine of which is immediately precipitated by silver nitrate. With potassium platinosochloride it yields a *salt*, ($Pt4A)PtCl_4$, pink needles, m. p. 127°, which is not acted on by Reiset's chloride I.

An attempt was made to prepare the two isomerides having the constitution ($Pt2A2NH_3)Cl_2$, but it only yielded gummy products which with potassium platinosochloride gave the same *salt*,

$$(Pt2A2NH_3)PtCl_4,$$

lilac needles, m. p. 151°. W. G.

The Nitrile and Sulphonamide of Thiodiacetic Acid. NILS VON ZWEIGBERGK (*Ber.*, 1912, 45, 3337—3338).—Dry hydrogen sulphide and ammonia are led into an ethereal solution of chloroacetonitrile until the solution, which first becomes warm, begins to cool. After collecting the precipitated ammonium chloride and concentrating the filtrate, white, rhombic tablets of the *nitrile* of thiodiacetic acid, $S(CH_2\cdot CN)_2$, are obtained, m. p. 45·5—46·5°. Acetone may be used instead of ether as solvent. The substance cannot be obtained by the action of phosphoric oxide on ammonium thiodiacetate.

If, instead of proceeding as above, an ammoniacal, alcoholic solution of chloroacetonitrile is saturated with hydrogen sulphide, yellowish-white leaflets of the *sulphonamide* of thiodiacetic acid, $S(CH_2\cdot CS\cdot NH_2)_2$, m. p. 124—125°, are obtained. T. S. P.

Constitution of the Compound known as Phorononitrile, and on Some Other Derivatives of Phoronic and Mesitylic Acids. J. MILIKAN (*Rec. trav. chim.*, 1912, 31, 287—298).—The true nitrile of phoronic acid should have the formula $C_{11}H_{16}ON_2$, whereas the so-called nitrile discovered by Pinner (A., 1881, 796) has the formula $C_{11}H_{18}O_2N_2$. Applying the conclusions drawn by Anschütz in the case of mesitonic acid (A., 1888, 1272) to the present question, the relation of these nitriles to phorone should be represented thus: Phorone, $CMe_2{:}CH\cdot CO\cdot CH{:}CMe_2$. Nitrile, $CN\cdot CMe_2\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot CN$. Amide,

$$NH_2\cdot CO\cdot CMe_2\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot CO\cdot NH_2.$$

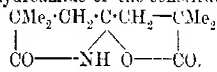
So-called nitrile, $\begin{array}{l} CMe_2\cdot CH_2\cdot C\cdot CH_2\cdot CMe_2 \\ | \qquad\quad\ \ / \ \backslash \qquad | \\ CO\text{——}NH\ \ NH\text{–}CO \end{array}$

As the direct addition of hydrogen cyanide to such an unsaturated ketone as phorone would be extremely difficult, an attempt has been made to prepare the amide. *Methyl phoronate*, $C_{13}H_{22}O_5$, obtained in white needles, m. p. 30°, by the action of methyl alcohol and sulphuric acid on phoronic acid, was heated for some hours with alcoholic ammonia in a sealed tube, when, instead of the expected amide, the so-called phorononitrile was the product, m. p. 326—327°.

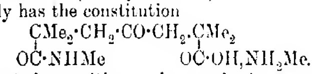
As the amide group is in the favourable γ position with respect to the ketone group, it is assumed that the expected amide has lost water and that the phoronouitrile is a di-lactam or an anhydrodiamide of the above constitution. It is possible to replace the hydrogen attached to the nitrogen in compounds of this structure, and, in fact, *diacetylanhydrophoronodiamide*, $C_{15}H_{22}O_4N_2$, m. p. 89—90°, has been obtained by the action of acetic anhydride. The compound is also very stable and dissolves in cold concentrated nitric acid, yielding a crystalline mass which is probably an additive product with the acid, and from which, water recovers the material unchanged.

Analogous anhydrodiamides are the imidopimelimide of Marckwald (A., 1888, 677; compare also Volhard, A., 1892, 433) and the ketodi-imide of β-acetylglutaric acid of Emery (A., 1897, i, 325).

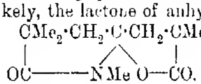
Pinner's phoronimide (*loc. cit.*) also yields the anhydrodiamide on heating with ammonia, and, accepting Anschütz's di-lactone structure for the parent substance phoronic anhydride, it is probable that the imide is a lactone-anhydroamide of the constitution



Methyl phoronate and the di-lactone have also been heated with methylamine, the product being *anhydrophoronodimethyldiamide*, $C_{11}H_{22}O_2N_2$, m. p. 136—137°, which is much less stable than the unsubstituted anhydrodiamide, since it readily loses methylamine on warming with potassium hydroxide. The *product* of the action of methylamine on the di-lactone in the cold has the formula $C_{13}H_{26}O_4N_2$ and m. p. 116—118°, and from analogy to the fact that ammonia forms with hydrochelidonodi-lactone (Volhard, *loc. cit.*) and with β-acetylglutarodilactone (Emery, *loc. cit.*) ammonium salts of amino-acids, it probably has the constitution



It decomposes at its melting point, and the *product*, $C_{12}H_{19}O_3N$, m. p. 110°, is, most likely, the lactone of anhydrophoronomethylamide,



Methyl mesitylate, $C_9H_{15}O_3N$, has also been prepared in colourless needles, m. p. 119—120°. J. C. W.

The Formation of Metallic Nitrides from Thiocyanates and Cyanides. ALEXANDER C. VOURNASOS (*Zeitsch. anorg. Chem.*, 1912, 77, 191—196. Compare A., 1911, ii, 600).—Aluminium, in the form of an impalpable powder, reduces many organic nitrogen compounds, with formation of the nitride; thus, with thiocarbamide, the reaction is $CS(NH_2)_2 + 2Al = Al_2N_2 + H_2S + H_2 + C$.

Potassium and ammonium thiocyanates, dried and mixed with aluminium powder, react if placed in a covered crucible and heated by the blowpipe according to the equation: $2KCNS + 2Al = {}_2S_2 + Al_2N_2 + 2C$, but a secondary reaction occurs to some extent between

the aluminium nitride, carbon, and potassium sulphide: $2K_2S + Al_2N_2 + 2C = Al_2S_3 + 2KCN + K_2S$. Washing the product with alcohol gives a residue consisting of aluminium and carbon. Boron reacts in a similar manner.

Magnesium reacts violently with thiocyanates, more quietly with cyanides: $2KCN + 3Mg = Mg_3N_2 + 2K + 2C$, the product containing free potassium, whilst some carbide is formed at higher temperatures.

Glucinum reacts quantitatively with cyanides: $3Gl + Hg(CN)_2 = Gl_3N_2 + Hg + 2C$, and calcium reacts in a similar manner. C. H. D.

The Supposed Case of Isomerism with Potassium Ferricyanide. OTTO HAUSER and E. BIESALSKI (*Ber.*, 1912, 45, 3516—3521).—The supposed green isomeride of potassium ferricyanide (compare Locke and Edwards, A., 1899, i, 407; Bellucci and Sabatini, A., 1911, i, 430) is simply the ordinary salt containing some Prussian-blue as impurity; the aqueous solution contains the Prussian-blue in collodial solution. An artificial mixture of potassium ferricyanide and Prussian-blue answers to all the reactions of the supposed green isomeride, and gives the same absorption and ultramicroscopic phenomena. The non-formation of the ferri-imido-ester (compare Bellucci and Sabatini, *loc. cit.*) from the green isomeride, or at all events its formation to a limited extent, is due to the catalytic effects of the decomposition product.

The above agrees with Piutti's observation (A., 1912, ii, 712) that the red and green forms have exactly the same absorption spectrum.

T. S. P.

Complex Compounds of Iron and the Formation of Nitroprusside. PAUL SCHWARZKOPF (*Abhandl. deut. naturwiss-med. Ver. Böhmen*, 1911, 3; Reprint 55 pp.).—The assumption that the formation of nitroprusside occurs according to two consecutive reversible reactions:

$$K_4FeCy_6 + NaNO_2 \rightleftarrows K_3Na(FeCy_5NO_2) + KCN \text{ and}$$
$$K_3Na(FeCy_5NO_2) + H_2O \rightleftarrows K_2(FeCy_5NO) + KOH + NaOH$$

has been tested by titrimetric estimation of the alkali present after equilibrium is reached, and the results when substituted into an equation derived to represent the conditions of the equilibrium, yield good constants. Considering the reactions from the ionic point of view, $(FeCy_6)'''' + (NO'_2) \rightleftarrows (FeCy_5NO_2)'''' + Cy'$ and $(FeCy_5NO_2)'''' + H_2O \rightleftarrows (FeCy_5NO)'' + 2OH''$, the first stage seems to imply a dissociation of the ferrocyanide ion into $(FeCy_5)'''$ and Cy'; this is quite probable as mercuric chloride in not too dilute solution of potassium ferrocyanide precipitates an iron ferrocyanide apparently indicative of a series of dissociations finally reaching the ferrous ion; similarly formaldehyde which is well known to combine with hydrocyanic acid, acts on a warm solution of potassium ferrocyanide, forming a deposit consisting of a mixture of ferrous and ferric hydroxides with a complex ferrocyanide. The power of mercuric chloride to remove cyanide ions from a solution should therefore accelerate the formation of nitroprusside by withdrawing the cyanide ion produced in the first stage of the action, and experimental investigation shows that it effects a very

considerable acceleration. It was not found possible to prepare compounds in which more than one (CN) group of potassium ferrocyanide is replaced by (NO).

It is also discovered that nitrous acid exerts an incomplete oxidising action on an acidic solution of potassium ferrocyanide and an incomplete reducing action on acidic solutions of potassium ferricyanide; in a similar manner it causes the oxidation of an ordinary ferrous salt and the reduction of a ferric one. D. F. T.

Preparation and Properties of Scandium Platinocyanide. N. A. Orlov (*Chem. Zeit.*, 1912, 36, 1407—1408).—The compounds of scandium which have hitherto been obtained leave it doubtful whether scandium must be classed with the cerium group or with the yttrium group of the rare earths. The double sulphate with potassium sulphate resembles the double sulphates of the cerium metals, whilst the weak basic properties of scandium, and the fact that copious precipitates are obtained when the salts are boiled with solutions of sodium thiosulphate or hydrofluosilicic acid, indicates its resemblance to the yttrium metals. The platinocyanides of the cerium metals are yellow, whilst those of the yttrium metals are red, and this should give a method of classifying scandium. Scandium platinocyanide was obtained by concentrating the solution obtained after collecting the precipitate of barium sulphate formed on mixing equivalent solutions of scandium sulphate and barium platinocyanide. Yellow crystals, which are very similar in appearance to cerium platinocyanide, separate from the solution, but a red, crystalline crust forms on the sides of the vessel. On drying, the yellow crystals become reddish- or orange-coloured. If the solution is evaporated to dryness on the water-bath a yellow residue is obtained, which becomes red on cooling. The reverse change from red to yellow takes place on heating. The yellow crystals have a composition corresponding with the formula $Sc_2(PtC_4N_4)_3,18H_2O$, whilst the red crystals have the formula

$$Sc_2(PtC_4N_4)_3,21H_2O.$$

T. S. P.

Some Metallic Salts and Complex Metallic Derivatives of Cyano-carboxylic Acids and their Esters. Lizzie Petterson (*J. pr. Chem.*, 1912, [ii], 86, 458—471).—An account of the preparation and properties of some metallic salts and derivatives of cyanoacetic and α-cyanopropionic acids.

By triturating cuprous oxide with a hot concentrated aqueous solution of cyanoacetic acid in the absence of air, a *cuprous* salt,

$$CN{\cdot}CH_2{\cdot}CO_2Cu,3CN{\cdot}CH_2{\cdot}CO_2H,H_2O$$

is obtained in small, white needles, which become green and melt at 119—120° when rapidly heated.

The *ferric* salt, $Fe_3(CO_2{\cdot}CH_2{\cdot}CN)_7(OH)_2,6H_2O$, prepared by the addition of ferric sulphate to a solution of barium cyanoacetate, forms deep, garnet-red prisms, m. p. 107°; the *cobalt*, *cupric*, and *silver* salts are also mentioned.

Hydroxymercuricyanoacetic acid, $OH{\cdot}Hg{\cdot}CH(CN){\cdot}CO_2H$, is obtained as a white, crystalline precipitate by shaking mercuric oxide for two days with an aqueous solution of cyanoacetic acid; the *sodium* and

barium salts are prepared in a similar manner from the corresponding salts of cyanoacetic acid; the *potassium* salt is prepared by the addition of potassium hydroxide to an aqueous solution of mercuric cyanide and potassium cyanoacetate.

The *methyl* and *ethyl* esters are formed by the interaction of mercuric acetate and the corresponding esters of cyanoacetic acid in methyl alcoholic solution.

Mercuric acetate reacts with ammonium cyanoacetate in aqueous solution, yielding the *compound*, $O<\begin{matrix}Hg\cdot CH(CN)\cdot CO_2\\ Hg\cdot CH(CN)\cdot CO_2\end{matrix}>Hg$, as a white, flocculent precipitate.

a-Hydroxymercuri-a-cyanopropionic acid, $OH\cdot Hg\cdot CMe(CN)\cdot CO_2H$, is a yellowish-white, crystalline substance obtained by the addition of a-cyanopropionic acid to a solution of mercuric oxide in excess of dilute acetic acid. F. B.

The Benzene Problem. KURT GEBHARD (*J. pr. Chem.*, 1912, [ii], 86, 540—545).—A repetition of the author's views on the structure of the benzene ring (A., 1912, ii, 242), together with a criticism of a recent paper by Liebig on this subject (A., 1912, i, 686). F. B.

Chemical Action of Light. III. Oxidation of Benzene Hydrocarbons. HERMANN SUIDA (*Monatsh.*, 1912, 33, 1255—1285).—The fact that the most easily isolable products of the autoxidation in light of benzene homologues are carboxy-acids is attributed to the relative instability of the intermediate products.

The most satisfactory source of light used was a quartz lamp, used at a distance of about 10 centimetres from the specimen of substance. The velocity of the first stage of the oxidation could be approximately measured by the amount of peroxide formation; this was estimated by the action on a solution of potassium iodide acidified with dilute sulphuric acid with titration of the liberated iodine some hours afterwards. The parallel formation of carboxylic acids was estimated previously by titration with $N/30$-potassium hydroxide solution; it appears that the amount of acid formed cannot be entirely due to the decomposition of the peroxide.

The results indicate that pure benzene is practically passive, but that the presence of thiophen causes peroxide formation. Methyl substituted benzenes undergo autoxidation when illuminated, and the action is accelerated by the presence of small quantities of nitrobenzene or of one of the nitrotoluenes. The oxidation of xylene occurs more than twice as rapidly as that of the toluenes, and *p*-xylene oxidises more rapidly than the ortho-isomeride. The oxidation of 4-nitro-*m*-xylene under the influence of light resembles that of *p*-nitrotoluene, but is feebler; this accords with the behaviour of these substances towards chromic acid; *p*- and *o*-nitrotoluenes are oxidisable by this reagent to the corresponding aldehydes, but 4-nitro-*m*-xylene in acetic anhydride solution containing sulphuric acid is oxidised, according to the conditions, to *4-nitro-m-tolualdehyde*, small, yellow rods, m. p. 64° (*phenylhydrazone*, m. p. 108°), or the corresponding *diacetate*,

$NO_2\cdot C_6H_3Me\cdot CH(OAc)_2$, yellow needles, m. p. 80—82°, together with some 4-nitro-*m*-toluic acid, m. p. 219—220°.

The results are discussed in relation to their theoretical bearing.

D. F. T.

Rational Preparation of Benzene Homologues. FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1912, [ii], 86, 518—520. Compare Rennie, T., 1881, 41, 33).—In the preparation of the homologues of benzene by the Friedel-Craft reaction, the alkyl haloids may be replaced with advantage by the esters of chlorocarbonic acid.

When aluminium chloride is added to a mixture of the aromatic hydrocarbon and chloro-ester, several alkyl groups are simultaneously introduced, whilst if the ester is added to a cooled mixture of the hydrocarbon and aluminium chloride, the main product consists of a hydrocarbon in which only one alkyl group has been substituted.

The preparation of toluene and xylene from methyl chlorocarbonate and benzene, of trimethylbenzene from toluene, and of diethylbenzene and diethyltoluene, is described.

The *iso*butyl and amyl esters of chlorocarbonic acid give better yields than the lower homologues.

F. B.

a-Phenyl-ββ-dimethylpropane, a New Amylbenzene. ARTUR BYGDÉN (*Ber.*, 1912, 45, 3479—3483).—The interaction of magnesium benzyl chloride and *tert.*-butyl bromide in boiling ether leads to the formation of *a-phenyl-ββ-dimethylpropane*, $CMe_3\cdot CH_2Ph$, b. p. 185·6—186·0°, $D_4^{18.3}$ 0·8581, $n_D^{18.3}$ 1·48837, a colourless liquid having a pleasant, aromatic odour resembling that of anisole.

C. S.

Influence of Light on the Rate of Polymerisation of Phenylbutadiene. HANS STOBBE and FRITZ REUSS (*Ber.*, 1912, 45, 3496—3498).—The formation of bisphenylbutadiene by different methods has been recorded by several investigators. The authors have performed parallel experiments, in darkness and in ordinary daylight, on phenylbutadiene in an atmosphere of carbon dioxide. The course of the polymerisation is followed by measuring the change in the refractive index. It is found that the polymerisation proceeds in the dark, but is considerably accelerated by light. Assuming that the quantity of the bimolecular form is proportional to the refractive index, the unexposed hydrocarbon contains 12—13% of bisphenylbutadiene and the insolated specimen 75—76%, after two and a-half months. The polymerisation appears to be complete after seven months.

C. S.

Action of Aniline on 1:3:5-Tribromo-2:4:6-tri-iodobenzene. CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Chem. Zentr.*, 1912, ii, 1275; from *Bul. Soc. Ştiinte Bucareşti*, 1912, 21, 23—26).—When this tribromotri-iodobenzene is heated with aniline it undergoes more extensive substitution than is the case with hexachlorobenzene (compare *ibid.*, 20, 621), and the resulting polyamines are more easily oxidised. Alcohol extracts from the product a *tribromoiodobenzene*, needles, m. p. 154—156°, the *aniline* salt of *glyoxylic*

acid, $C_8H_{11}O_4N$, yellowish-white leaflets, m. p. 173°, and also aniline hydrobromide and iodide, whilst the amorphous, dark blue, insoluble residue has the composition of an iodopenta-anilinobenzene.

J. C. W.

Rule of the Conservation of the Type in Benzene Substitutions. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1912, **31**, 267—280). When reviewing the introduction of further substituents into benzene rings which have already been once or twice substituted, only a few doubtful cases were found which were contrary to the rule that the position occupied is independent of the nature of the substituent. It is now shown that the bromination and the nitration of *o*-iodotoluene, the bromination of *o*-chlorotoluene, and the chlorination of *o*-chloronitrobenzene are no longer to be regarded as exceptions to the rule.

Hirtz (A., 1896, i, 531) assigned to the product obtained by brominating *o*-iodotoluene, "by analogy," the constitution

$$Me:I:Br = 1:2:4,$$

whereas Reverdin (A., 1898, i, 180) showed conclusively that the chief nitration product was $Me:I:NO_2 = 1:2:5$. The latter compound has now been reduced by means of iron powder, yielding the *iodotoluidine*, $Me:I:NH_2 = 1:2:5$, as unstable, white leaflets, m. p. 42°, which were diazotised with difficulty in hydrobromic acid solution, and converted into bromoiodotoluene, $Me:I:Br = 1:2:5$, b. p. 262—265°, $n_{14} = 1{\cdot}6484$. On the other hand, the direct bromination of *o*-iodotoluene (compare Hirtz, *loc. cit.*) was accomplished in the presence of iron powder, but the product was of a very complicated nature, although the main fraction boiled at 260—265°. Direct comparison of such liquids being impossible, it was sought to obtain crystalline nitro derivatives of them. The preparation from *o*-iodonitrotoluene, when heated with fuming nitric acid, gave 5-bromo-2:6-dinitrotoluene, m. p. 103°. The mixture from the direct bromination, when nitrated in acetic acid, gave a small number of yellowish-green crystals, a *bromoiododinitrotoluene*, m. p. 178—181°, which was the principal product when the highest fraction, b. p. 270—275°, was separately treated. The larger portion, however, remained in solution, and on dilution with water a product was obtained, m. p. 92—93°, which was shown to be a eutectic mixture of the above bromoiododinitrotoluene and the 5-bromo-2:6-dinitrotoluene. Assuming that only the 1:2:5-compound loses iodine on nitration, an estimation of the hydrogen iodide showed that this isomeride formed about 40% of the mixture. The 5-position is therefore entered to a preponderating extent by both the nitro-group and the bromine atom.

In the analogous case of the bromination of *o*-chlorotoluene it is most likely that the product is a mixture of all the possible isomerides, although it is not proved that the prevailing one is the 1:2:5. This one, however, predominates in the case of the nitration of *o*-chlorotoluene, as Wibaut will soon describe.

Cohen and Bennet (T., 1905, **87**, 323) obtained by the chlorination of *o*-chloronitrobenzene the isomerides $Cl_2:NO_2 = 1:4:2$ and $1:6:2$, and a further product which melted at 31° was said by them to be the 1:5:2 compound. The entry of chlorine into a position meta to

chlorine and para to a nitro-group is contrary to the conservation of type, and it is now shown that the doubtful product is most probably a eutectic mixture of the 1 : 4 : 2 and 1 : 6 : 2 isomerides. J. C. W.

Nitro-derivatives of 2 : 6-Dibromotoluene. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, **9**, 968—972. Compare A., 1912, i, 982).—A number of nitro-derivatives of 2 : 6-dibromotoluene have been prepared. The parent substance is obtained by replacing the amino-group in 6-bromo-*o*-toluidine (compare Friedländer, Bruckner, and Deutsch, A., 1912, i, 318) by bromine by the Sandmeyer method, and forms colourless crystals, m. p. 2°, and not as stated by Nevile and Winther (T., 1880, **37**, 429). By the action of nitric acid (D 1·45) this substance is converted into 2 : 6-*dibromo-3-nitrotoluene*, pale yellow crystals, m. p. 50°, and not 2 : 6-dibromo-4-nitrotoluene as stated by Nevile and Winther. Its constitution was proved by its formation from 6-bromoacet-*o*-toluidide. On nitration, this substance yields 6-*bromo-3-nitroacet*-o-*toluidide*, yellow crystals, m. p. 199°, converted by concentrated sulphuric acid into 6-*bromo-3-nitro*-o-*toluidine*, orange-yellow crystals, m. p. 144°. Exchange of the amino-group of this compound for bromine by the Sandmeyer reaction yields 2 : 6-dibromo-3-nitrotoluene, identical with the product obtained by nitration of 2 : 6 dibromotoluene. Potassium permanganate does not oxidise it to the corresponding benzoic acid derivative. Further nitration converts it into 2 : 6-*dibromo-3 : 5-dinitrotoluene*, colourless crystals, m. p. 161°. Heating with alcoholic ammonia at 100° yields 6-bromo-3 : 5-dinitro-*o*-toluidine, yellow crystals, m. p. 200°; its acetyl derivative forms colourless crystals, m. p. above 300°; at 150° the product is 3 : 5-*dinitro*-1 : 2 : 6-*tolylenediamine*, light brown crystals, m. p. 298°; the corresponding acetyl derivative forms colourless crystals, decomposing above 300°. At 150° an alcoholic solution of methylamine converts 2 : 6-dibromo-3 : 5-dinitrotoluene into 3 : 5-*dinitro*-1 : 2 : 6-*tolylenedimethyldiamine*, orange-red crystals, m. p. 216°.

Nitration of 2-bromoaceto-*p*-toluidide produces 2-*bromo-5-nitroaceto*-p-*toluidide*, pale yellow needles, m. p. 120°, converted by concentrated sulphuric acid into 2-*bromo-5-nitro*-p-*toluidine*, orange-red needles, m. p. 165°, which is converted by diazotisation into 2-bromo-5-nitrotoluene, identical with that obtained from 6-bromo-3-nitro-*o*-toluidine.

Replacement of the amino-group in 2-bromo-5-nitro-*p*-toluidine by bromine by the Sandmeyer reaction yields 2 : 4-*dibromo-5-nitrotoluene*, colourless needles, m. p. 85°. Nitration with nitric and sulphuric acids converts this substance into 2 : 4-dibromo-3 : 5-dinitrotoluene, m. p. 130° (compare Davis, T., 1902, **81**, 873), which with alcoholic ammonia at 150° yields 3 : 5-dinitro-1 : 2 : 4-tolylenediamine (compare A., 1904, i, 566). A. J. W.

Preparation of Anthracenemonosulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 251695).—The preparation of anthracenemonosulphonic acids has previously been

attended with difficulty; it is now found to proceed smoothly if the sulphonation is carried out in the presence of glacial acetic acid.

A solution of anthracene (300 parts) in acetic acid (600 parts) is cooled and slowly treated with chlorosulphonic acid (200 parts), the mixture is rapidly heated to 95°, and maintained at this temperature during five hours; the clear olive-green solution is treated with water (5000 parts), and the insoluble residue subsequently treated with more water (4500 parts) at 40°. The anthracene-α sulphonic acid (in 5% yield) is precipitated from the filtrate with salt, whilst the residue on treatment with a large volume of hot water furnishes anthracene-β-sulphonic acid in over 30% yield. F. M. G. M.

Tridiphenylylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1912, 45, 3171—3183).—The tridiphenylylmethyl discovered earlier (Schlenk, Weickel, and Herzenstein, A., 1910, i, 236) is a mixture of two isomerides.

By a modification of the method of the earlier workers good yields of the tridiphenylylcarbinol could be obtained. 4-Bromodiphenyl in ethereal solution was converted by the action of magnesium and successive quantities of iodine into the corresponding organo-magnesium compound which reacted with *p*-bisdiphenylyl ketone, producing a mixture of α- and β-tridiphenylylcarbinol, together with some *p*-tridiphenylylmethane and *p*-bisdiphenyl. p-*Tridiphenylylmethane*, obtainable also by the reduction of the mixture of α- and β-tridiphenylylcarbinols, forms colourless crystals, m. p. 241—242° (corr.), and when recrystallised from benzene tenaciously retains benzene of crystallisation even to the m. p.; p-*bisdiphenyl* forms inodorous leaflets, m. p. 318—319° (corr.).

The isomeric carbinols, the relative proportions of which varied considerably in different experiments, could be separated by fractional recrystallisation of the mixture from ether, or by converting into a mixture of the chlorides and then recrystallising from benzene. α-*Tridiphenylylmethylcarbinol*, the less soluble isomeride, has m. p. 212° (corr.), whilst the β-compound forms leaflets, m. p. 199—200° (corr.); both carbinols, at a concentration of 1 : 60,000, in a mixture of acetic and sulphuric acids give an absorption band from 440 to 510 μμ. The action of acetyl chloride or, better, of hydrogen chloride on the benzene solution converts the carbinols into the corresponding chlorides: α-*tridiphenylylmethyl chloride*, needles, m. p. 200° (corr.); β-*chloride*, m. p. 187—188° (corr.). The two chlorides are convertible by the action of copper powder on the benzene solution into the corresponding tridiphenylylmethyls; α-*tridiphenylylmethyl*, $C(C_6H_4Ph)_3$, is a dark green, crystalline powder, the solution of which is brownish-red, and at a concentration of 1 : 5000 shows an absorption band from 430 μμ to the ultra-violet; the molecular weight in benzene solution was 499, the theoretical being 471.

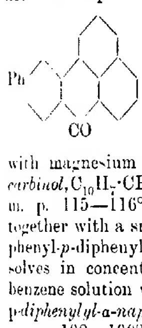
β-*Tridiphenylylmethyl* forms dark green needles, and gives a deep blue solution, which shows an absorption band (at a concentration 1 : 6000) extending from 600 to 640 μμ; the molecular weight in benzene was 518. The two tridiphenylylmethyls easily undergo

atmospheric oxidation, producing the α- and *β-tridiphenylylmethyl peroxides*, m. p. 213° (corr.) and 198° respectively.

Experiments were made to ascertain whether so-called triphenylmethyl can be observed to dissociate into the unimolecular condition. Gomberg and Cone (A., 1904, i, 658) obtained molecular weights in phenol solution indicating a dissociation, but this result was due to chemical interaction between solvent and solute with the formation of *p*-hydroxytetraphenylmethane, m. p. 282°, and triphenylmethane. By determining the alteration of m. p. and b. p. successively with the same benzene solution, it is now shown that the molecular weight is the same at both temperatures, and is only a little lower than that calculated for the bimolecular condition. The alteration in the colour of solutions of triphenylmethyl on warming is, therefore, probably not due to dissociation. D. F. T.

Phenyldiphenylylnaphthylmethyl. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÙS (*Ber.*, 1912, 45, 3183—3188).—The authors have succeeded in preparing triarylmethane compounds containing an asymmetric carbon atom.

p-*Diphenylyl α-naphthyl ketone*, $C_6H_4Ph\cdot CO\cdot C_{10}H_7$, obtained by the action of naphthoyl chloride on diphenyl in carbon disulphide solution under the influence of aluminium chloride, forms plates, m. p. 142° (corr.); when heated with aluminium chloride at 140—145°, it condenses to *phenylbenzanthrone* (annexed formula), golden-yellow plates, m. p. 178—179° (corr.), which gives a fluorescent red solution in concentrated sulphuric acid. The above diphenylyl naphthyl ketone reacts



with magnesium phenyl iodide giving *phenyl-*p*-diphenylyl-α-naphthylcarbinol*, $C_{10}H_7\cdot CPh(C_6H_4Ph)\cdot OH$, prisms (with ether of crystallisation), m. p. 115—116° (corr.), m. p. when ether-free 164—165° (corr.), together with a small amount of a *substance*, m. p. 197—198°, possibly phenyl-*p*-diphenylyl-α-naphthylmethane. The carbinol, which dissolves in concentrated sulphuric acid to a violet solution, reacts in benzene solution with hydrogen chloride with the formation of *phenyl-*p*-diphenylyl-α-naphthylmethyl chloride*, a colourless, crystalline powder, m. p. 198—199° (corr.). In an atmosphere of carbon dioxide the chloride is reduced by copper powder to *phenyl-*p*-diphenylyl-α-naphthylmethyl*, an apparently homogeneous product (compare preceding abstract); this dissolves in benzene to a brown solution, and from the fact that the solution, after most of its colour has been destroyed by atmospheric oxidation, recolorises to some extent, it is suggested that, unlike tridiphenylmethyl, the present substance is not completely dissociated into the active unimolecular condition; the fresh solution (concentration 1 : 5000) shows a broad absorption band from the violet end of the spectrum to 480μμ, and a small band in the yellow; the fresh solution of the corresponding phenyl-*p*-diphenylyl-α-naphthylcarbinol in sulphuric acid gives an absorption spectrum with a band extending from 480μμ half way into the green. Solutions of the above phenyl-*p*-diphenylyl-α-naphthylmethyl are

oxidised by the atmosphere to the *peroxide*, $(C_{29}H_{21})_2O_2$, a colourless, crystalline powder, m. p. 158° (corr., decomp.).

Although triphenylmethyl chloride, by the action of menthol in pyridine solution, can be converted into *triphenylmethyl* l-*menthyl ether*, m. p. 137—138° (corr.), similar treatment of phenyl-*p*-diphenylyl-α-naphthylmethyl chloride produced only the corresponding carbinol. It was also found impossible to prepare the camphorate or camphor-sulphonate. The chloride of the carbinol will not react with nicotine or coniine, and the product obtained by replacing the halogen by the amino-group is not basic in properties. The most promising method for the resolution of the asymmetric carbinol into its enantiomorphous constituents appears to depend on the active *amyl ether* which has been obtained in the crystalline state. D. F. T.

Reduction of Aromatic Alcohols with Aliphatic Alcohols. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÚS (*Ber.*, 1912, **45**, 3188—3193 *).—By using sulphuric acid as solvent, the reduction of aromatic secondary and tertiary carbinyl chlorides by aliphatic alcohols, already observed in special cases (for example, Kauffmann and Fritz, A., 1909, i, 99), becomes a fairly general reaction. Triphenylcarbinol and triphenylmethyl chloride, in a mixture of equal volumes of alcohol and sulphuric acid, undergo reduction to triphenylmethane, the action being represented: $CPh_3{\cdot}SO_4H + EtOH = CHPh_3 + CH_3{\cdot}CHO + H_2SO_4$; the ethyl alcohol can be replaced by methyl alcohol. In a similar manner tridiphenylylmethane and diphenylmethane can be obtained from tridiphenylylmethyl chloride or tridiphenylylcarbinol and benzhydrol respectively. The reaction fails with the naphthalene-carbinols, and also in cases where the sulphuric acid itself can cause dehydration or other effects, as, for example, with αβ-diphenylethyl alcohol, which yields stilbene.

The reduction of triphenylmethyl in ethereal solution by hydrogen and platinum black produces only triphenylmethane.

The oxidation of triphenylmethane to the corresponding carbinol can be quantitatively effected by boiling nitric acid, D 1·33 (compare Schwarz, A., 1909, i, 561).

A diagram is given for an apparatus designed for the preparation of fairly large quantities of triphenylmethyl and analogous compounds.

Endeavours to prepare a "mixed" ethane derivative by the interaction of magnesium triphenylmethyl chloride and tridiphenylylmethyl chloride produced only a mixture of triphenylmethyl and tridiphenylylmethyl; also no crystalline product could be obtained from the same Grignard reagent and phenylfluorenyl chloride. D. F. T.

Valency of Carbon, Arsenic, and Silicon. WILHELM SCHLENK (*Annalen*, 1912, **394**, 178—223).—[With LEOPOLD MAIR.]—The deepening of the colour of a solution of triphenylmethyl by warming has been attributed to the shifting of the equilibrium of the system $CPh_3{\cdot}CPh_3 \rightleftharpoons 2CPh_3$ from left to right. Gomberg has shown by the cryoscopic method that triphenylmethyl in cold benzene exists almost entirely as hexaphenylethane. The authors now show by the ebullio-

* and *Anal. Fis. Quim.*, 1212, **10**, 449—454.

scopic method that at its b. p. the solution contains about 25% of triphenylmethyl.

Since triphenylmethyl peroxide and diphenylenephenylmethyl oxide (diphenylfluorene ether; Kliegl, A., 1905, i, 187) are comparatively stable substances, the authors hoped to prepare triphenylmethyl oxide, $(CPh_3)_2O$, from chlorotriphenylmethane by the action of silver oxide or of the sodium derivative of triphenylcarbinol. The products in both cases, however, are triphenylcarbinol and resinous substances.

[With C. BORNHARDT.]—The same products are also obtained by the oxidation of triphenylmethyl in glacial acetic acid or acetone by chromic acid or potassium permanganate.

After keeping triphenylmethyl and sulphur in carbon disulphide in darkness for six to eight weeks, the hydrocarbon is completely converted into an inseparable mixture of triphenylmethyl polysulphides.

A benzene solution of triphenylmethyl and an alcoholic ethereal solution of diazomethane react to form *hexaphenylpropane*,

$$CPh_3\cdot CH_2\cdot CPh_3,$$

a more complete description of which is promised.

[With JULIUS RENNING.]—By heating a benzene solution of phenylxanthenol chloride, prepared by Gomberg's method (A., 1910, i, 56), with copper-bronze on the water-bath, *phenylxanthyl*,

$$C_6H_4<{CPh \atop O}>C_6H_4,$$

is obtained. It forms brown crystals which disintegrates to a yellow powder at 60° in carbon dioxide, and is shown to be present in the unimolecular form to the extent of about 82% in boiling 1—2% benzene solution by the ebullioscopic method. *Phenylthioxanthyl*, $C_6H_4<{CPh \atop S}>C_6H_4$, prepared in a similar manner from phenylthioxanthenol chloride (Gomberg, A., 1910, i, 869), is a brownish-red, crystalline powder, and is present in the unimolecular form o the extent of about 14% in cold benzene. *Phenylanthronyl*,

$$C_6H_4<{CPh \atop CO}>C_6H_4,$$

is a yellow, crystalline powder; a 1—2% benzene solution contains in the cold about 33% of the unimolecular form. *Diphenyl-a-naphthylmethyl*, $C_{10}H_7\cdot CPh_2$, obtained by boiling *chlorodiphenyl-a-naphthylmethane*, m. p. 163°, with copper bronze in petroleum, b. p. 60—75°, in an atmosphere of carbon dioxide, is a greyish-black powder; a 2—3% solution in cold benzene contains about 59% of the unimolecular form. *Phenyl-p-diphenylyl-a-naphthylmethyl*,

$$C_6H_4Ph\cdot CPh\cdot C_{10}H_7,$$

prepared in a similar manner from *chlorophenyldiphenylyl-a-naphthylmethane*, m. p. 194·5°, is an olive-brown powder; a 1—3% solution in cold benzene contains the unimolecular form almost entirely.

[With LEOPOLD MAIR.]—p-*Anisyldiphenylenecarbinyl chloride*,

$${C_6H_4 \atop C_6H_4}>CCl\cdot C_6H_4\cdot OMe,$$

m. p. 149—151°, prepared by treating fluorenone with magnesium p-anisyl iodide in ether, decomposing the product in the usual manner,

and saturating a cold ethereal solution of the resulting carbinol with hydrogen chloride, reacts with copper-bronze in boiling benzene in an atmosphere of carbon dioxide to form *di-p-anisylbisdiphenylene-ethane*, $C_{40}H_{30}O_2$, m. p. 170—190° (decomp.) in open tube, 227—230° in carbon dioxide in a closed tube. It is a white, crystalline powder, stable in air, and forms solutions which become brown by warming and almost colourless again by cooling; its solution in benzene absorbs oxygen and yields the *peroxide*, $C_{40}H_{30}O_4$, m. p. 192°, colourless prisms.

[With ANNA HERZENSTEIN.]—The formation of triarylmethyls by the action of metals on solutions of triarylcarbinyl chlorides bears some resemblance to the elimination by one metal of another from a solution of its salts. In fact, when equal molecular quantities of triphenylmethyl and of phenyldidiphenylylcarbinyl chloride are brought together in benzene, the colour of the solution quickly darkens in consequence of the liberation of red phenyldidiphenylylmethyl by the yellow triphenylmethyl. Still more striking is the reaction which occurs when a benzene solution of phenylnaphthyldiphenylylcarbinyl chloride is added slowly to a solution of triphenylmethyl; each drop produces, with the rapidity of an ionic reaction, the deep reddish-brown coloration of phenyldiphenylylnaphthylmethyl.

[With GEORG RACKY and C. BORNHARDT.]—Attempts to prepare tervalent carbon derivatives containing radicles other than aryl groups show that such substances are not formed or usually exist in the dimolecular state; thus Wieland's benzpinacone diphenyl ether exists as such; only at high temperatures does it change to phenoxydiphenylmethyl (A., 1911, i, 851). The action of metals on chlorides of the type CAr_2RCl should yield hydrocarbons CAr_2R. When R is methyl or other alkyl group containing CH, however, the chloride cannot be isolated, since it spontaneously loses hydrogen chloride with the formation of diarylolefines. *Diphenyl*-tert.-*butylcarbinyl chloride*, $CPh_2Cl\cdot CMe_3$, m. p. 103—106°, large, colourless crystals, can be obtained by the interaction of magnesium phenyl bromide and ethyl trimethylacetate in ether, the product, isolated in the usual manner being saturated in ether with hydrogen chloride and finally boiled with acetyl chloride. By boiling in xylene with sodium, the chloride yields *diphenyldi*-tert.-*butylethane*, $CMe_3\cdot CPh_2\cdot CPh_2\cdot CMe_3$, which has no tendency to dissociate into the tervalent carbon derivative. *βββ-Trichloro-α-bromo-αα-diphenylethane*, $CPh_2Br\cdot CCl_3$, m. p. 87·5°, colourless crystals, obtained by treating the trichlorodiphenylethane with an excess of bromine, loses chlorine and bromine by treatment with metals.

By treatment with liquid nitrogen peroxide, tetraphenylethylene in chloroform yields *pp'-dinitrotetraphenylethylene*,

$$NO_2\cdot C_6H_4\cdot CPh\mathpunct{:}CPh\cdot C_6H_4\cdot NO_2,$$

m. p. 180—190°, citron-yellow crystals. In boiling nitrobenzene the two substances do not react. Bis-diphenylene-ethylene in chloroform and nitrogen peroxide yield *dinitrobisdiphenylene-ethane*,

$$\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>C(NO_2)\cdot C(NO_2)<\!\!\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array},$$

colourless crystals, which is stable, but decomposes by melting (178°) and yields fluorenone and nitric oxide, whilst by heating with phenol it yields nitrophenol and bisdiphenylene-ethylene.

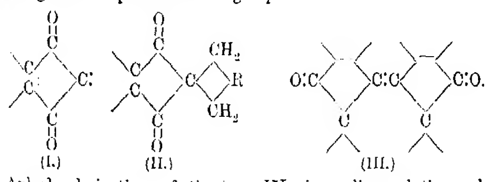
Tetradiphenylylethylene, which is obtained readily by boiling *diphenylyl ketochloride*, $CCl_2(C_6H_4Ph)_2$, m. p. 136°, in xylene with copper bronze, reacts with nitrogen peroxide in chloroform to form a blue substance, which rapidly decomposes, yielding diphenylyl ketone.

[With GEORG RACKY.]—The vapour density of arsenic disulphide at about 900° corresponds with the formula As_2S_2. The authors' experiments on the molecular weight of arsenic di-iodide in boiling benzene lead conclusively to the formula As_2I_4 (compare Hewitt and Winmill, T., 1907, **91**, 962). The molecular weight of tetraphenylcacodyl in boiling benzene corresponds with the formula As_2Ph_4. Consequently there is no evidence of the existence of bivalent arsenic compounds.

[With JULIUS RENNING.]—Silicon tetrachloride in ether is treated with magnesium phenyl bromide (2 mols.) and subsequently with magnesium methyl iodide. After treatment with water, the mixture is fractionally distilled, whereby *diphenylsilicoethylene*, $SiPh_2{:}CH_2$, is obtained. It is a colourless, odourless liquid, b. p. 266—268°/720 mm., which does not react with bromine or decolorise alkaline potassium permanganate. C. S.

Spirans. VI. Some Properties of the Spiran Carbon Atom. DAN RADULESCU (*Chem. Zentr.*, 1912, ii, 1363—1366; from *Bul. Soc. Stiinte Bucaresti*, 21, 32—58. Compare A., 1912, i, 179).—The influence of the spiran carbon atom on the stability of, and on the conditions for the formation of, the two rings which it connects, and also on the reactivity of single members of the rings, is discussed. No steric hindrance exists which prevents the closing of spiran rings; in fact, spirans with five or six atoms in the ring are more stable than analogous compounds with open chains, so that the tendency is to form closed rings. The behaviour of the spiran carbon atom in strained ring systems has been studied in the case of *cyclo*propane-*cyclo*pentane-2 : 5-dione-1 : 1-spiran-3 : 4-dicarboxylic acid and its derivatives. The stability of the trimethylene ring is scarcely lessened by the spiran carbon atom.

The chromophoric properties of the rings are also affected by the quaternary system of the spiran carbon atom; the two spiran bonds in one ring act like a double link on the other ring. The group II is a stronger chromophore than the group I.

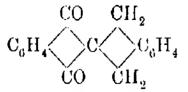


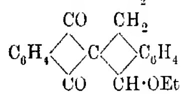
(I.) (II.) (III.)

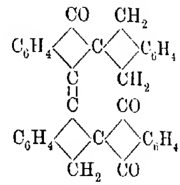
Anhydro-derivatives of the type III give yellow solutions which

with strong alkalis become blue. Carminic acid develops the same colour with very concentrated, strong bases, and has an absorption spectrum which is almost identical with that of compounds of this type.

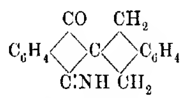
Fecht's indan-1 : 3-dione-indan-2 : 2-spiran (xylylenediketohydrindene) (A., 1907, i, 906) is found to be impure. Repeated solution in benzene and precipitation with light petroleum separates from it *anhydrobis-indan-1 : 3-dioneindan-2 : 2-spiran*, $C_{34}H_{22}O_8$, (V), in pale yellow flakes, m. p. 256—257°, which give with phenylhydrazine the brownish-red hydrazone of Fecht's spiran. A very dilute alcoholic solution develops an intense indigo colour with a drop of concentrated potassium hydroxide, whereas the pure indan-1 : 3-dione-indan-2 : 2-spiran (IV) gives no coloration. The latter forms golden-yellow, thick prisms, m. p. 149°, and gives a violet colour to concentrated sulphuric acid. The ethereal mother liquors from this compound still contain *indan-1 : 3-dione-1-ethoxyindan-2 : 2-spiran*, $C_{19}H_{16}O_3$, (VI), which forms yellow prisms, m. p. 199—200°, and imparts a red colour to sulphuric acid, but is not affected by alkalis.

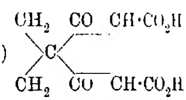
(IV.) 

(VI.) 

(V.) 

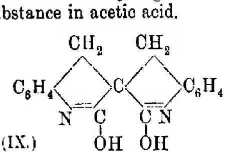
1-*Imino-3-indanoneindan-2 : 2-spiran*, $C_{17}H_{13}ON$, (VII), obtained by heating the spiran (IV) with alcoholic ammonia, separates in brick-red flakes.

(VII.) 

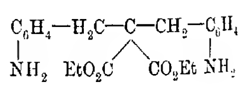
(VIII.) 

cyclo*Propanecyclopentanedione-1 : 1-spiran-3 : 4-dicarboxylic acid*, (VIII), from ethyl *cyclo*propane-1 : 1-dicarboxylate, ethyl succinate, and sodamide, is converted at 180—200° or by heating with acetic anhydride into the *anhydride*, $C_9H_6O_5$, small, white needles.

Bisdihydroxyquinoline-3 : 3-spiran (*bisdihydrocarbostyrylspiran*), $C_{17}H_{14}O_2N_2$, (IX), from the reduction of ethyl di-*o*-nitrobenzyl-malonate, sublimes above 360° in colourless, shining flakes, which dissolve when hydrogen bromide is passed into a suspension of the substance in acetic acid.



(IX.)



(X.)

When the mother liquors from the reduction are treated with

ammonia, the reddish primary product of the reaction, the *amino*-ester (X), separates out. It readily loses alcohol, forming the spiran.

Ethyl di-p-*nitrobenzylmalonate*, $C(CH_2 \cdot C_6H_4 \cdot NO_2)_2(CO_2Et)_2$, white needles, m. p. 171°, is the chief product when ethyl dibenzylmalonate is nitrated by fuming nitric acid in glacial acetic acid.

J. C. W.

Stereochemistry of Quinquevalent Nitrogen. I. Formation and Decomposition of the Quaternary Ammonium Bases and Salts. SHIGERU KOMATSU (*Mem. Coll. Sci. and Eng., Kyoto Imp. Univ.*, 1912, **3**, 371—426).—The author has prepared a long series of quaternary ammonium compounds, and finds m. p.'s for the iodides which generally show considerable divergence from those previously stated by Jones and by Wedekind. In the thermal decomposition of the hydroxides it is observed that in the series $HO \cdot NPh(CH_2Ph)XY$ the benzyl group is always the one to be eliminated; with the series $HO \cdot NPh(C_3H_5)XY$, if X and Y are smaller groups than the allyl, the last undergoes scission, but if one is larger and the other smaller than the allyl, the smaller of X and Y becomes removed. Apart from these two classes it is found that, as a general rule, the smallest group is always left attached to the nitrogen atom.

The following tertiary bases and derivatives were obtained. Dimethylaniline gives a *picrate*, needles, m. p. 154—155°, and combines with mercuric chloride giving a yellow *compound*, crystallising in needles, also a basic *compound*, $O(Hg \cdot NMe_2PhCl)_2$, pearly scales, and a *double* salt, $NMe_2Ph,HCl,HgCl_2$, colourless needles. Methylethylaniline gives a *picrate*, prisms, m. p. 121—122°; *ferrocyanide*, colourless crystals, and combines with mercuric chloride producing a colourless, scaly basic *compound*, $O(Hg \cdot N \cdot PhMeEtCl)_2$, and a *double* salt, colourless needles. Methylallylaniline forms a picrate, m. p. 81—82°, and *ferrocyanide*, colourless crystals. Methylpropylaniline gives a *picrate*, m. p. 103—104°; *ferrocyanide*, colourless. Methyl-*n*-butylaniline, b. p. 225—230°, forms a *picrate*, rhombic needles, m. p. 141—142°; *ferrocyanide*, light green, crystalline powder. Methyl*iso*butylaniline yields a *picrate*, plates, m. p. 99—100°, and *ferrocyanide*, colourless. Methyl*iso*amylaniline forms a *picrate*, m. p. 93—94°, and *ferrocyanide*, light green. Benzylmethylaniline gives a *picrate*, rhombic prisms, m. p. 101—101·5°; *ferrocyanide*, colourless; colourless *double* salt, $(NMePh \cdot CH_2Ph,HCl)_2CdCl_2$, with cadmium chloride, and with mercuric chloride a mixture of a yellow *substance* (which on exposure to air is slowly converted into a blue *substance*, m. p. about 160°), a basic *substance*, crystallising in white needles (composition analogous to that of the basic substances above), and a *double* salt, $(NMePh \cdot CH_2Ph,HCl)_2,HgCl_2$, colourless needles. Ethylallylaniline gives a *picrate*, prisms, m. p. 98—99°, and *ferrocyanide*, colourless. Ethyl-*n*-propylaniline forms a *picrate*, crystalline powder, m. p. 94—95°, and *ferrocyanide*, colourless. Ethyl-*n*-butylaniline gives a *picrate*, rhombic prisms, m. p. 89—90°, and *ferrocyanide*, colourless. Ethyl*iso*butylaniline yields a *picrate*, crystals, m. p. 91—92°, and *ferrocyanide*, light green, crystalline powder. Ethyl*iso*amylaniline forms a *picrate*, rhombic prisms, m. p. 103—104°, and

ferrocyanide, light green, crystalline powder. Benzylethylaniline gives a picrate, rhombic prisms, m. p. 110—111°; *ferrocyanide*, light green, crystalline powder, a *double* salt (colourless needles) with cadmium chloride, and with mercuric chloride a colourless, crystalline basic *substance* and a *double* salt (needles), $(NEtPh{\cdot}CH_2Ph,HCl)_2,HgCl_2$. Diethylaniline, *picrate*, m. p. 135—136°.

The m. p. of each of the above picrates, as also of most of the iodides below, was also determined by the Kuhara-Chikashigé method (A., 1900, ii, 260), the results differing occasionally by several degrees from those obtained by the ordinary method.

The following quaternary compounds were examined:

Phenylbenzyldimethylammonium iodide, m. p. 141—142° (compare Jones, T., 1903, **83**, 1409), obtained from dimethylaniline and benzyl iodide; *platinichloride*, needles, m. p. 164—165°; the *hydroxide* when heated decomposes, giving dimethylaniline. Phenylbenzylmethylethylammonium iodide, m. p. 135—136° (compare Jones, T., 1904, **85**, 224; Fröhlich, A., 1910, i, 375), from methylethylaniline and benzyl iodide; *platinichloride*, needles, m. p. 160·5—161°; the *hydroxide* decomposes, giving methylethylaniline. Phenylbenzylmethylallylammonium iodide, rhombic prisms, m. p. 128—129° (compare Jones, T., 1905, **87**, 1721; Wedekind, A., 1899, i, 351), obtained from methylallylaniline and benzyl iodide, or from benzylmethylaniline and allyl iodide; *platinichloride*, needles, m. p. 133—134°; the *hydroxide* when decomposed yields methylallylaniline. Phenylbenzylethyl-*n*-propylammonium iodide, prisms, m. p. 143°, from methyl-*n*-propylaniline and benzyl iodide; *platinichloride*, needles, m. p. 159—160°; the *hydroxide* on decomposition gives methyl-*n*-propylaniline. Phenylbenzylmethyl*iso*butylammonium iodide, prisms, m. p. 124—125°, obtained from methyl*iso*butylaniline and benzyl iodide; *platinichloride*, needles, m. p. 147—148°; the *hydroxide* on decomposition gives methyl*iso*butylaniline. *Phenylbenzylmethyl*-n-*butylammonium iodide*, needles, m. p. 132—133°, obtained from methyl-*n*-butylaniline and benzyl iodide; *platinichloride*, needles, m. p. 139—140°; the *hydroxide* on decomposition gives methyl-*n*-butylaniline. Phenylbenzylmethyl*iso*amylammonium iodide, from methyl*iso*amylaniline and benzyl iodide, needles, m. p. 137—138° (compare Thomas and Jones, T., 1906, **89**, 280); *platinichloride*, needles, m. p. 149—150°; the *hydroxide* on decomposition gives methyl*iso*amylaniline. Phenyldibenzylmethylammonium iodide, m. p. 105—106° from benzylmethylaniline and benzyl iodide (compare Jones, T., 1903, **83**, 1410); *platinichloride*, needles, m. p. 131—132°; the *hydroxide* on decomposition yields benzylmethylaniline. *Phenylbenzylethyl*-n-*propylammonium iodide* from ethyl-*n*-propylaniline and benzyl iodide, prisms, m. p. 105—106°; *platinichloride*, needles, m. p. 146—147°; the *hydroxide* on decomposition yields ethyl-*n*-propylaniline.

Phenylbenzylethylallylammonium iodide, obtained from ethylallylaniline and benzyl iodide, prisms, m. p. 106·5°; *platinichloride*, m. p. 138—139°. Phenyldimethylallylammonium iodide, from dimethylaniline and allyl iodide, prisms, m. p. 84—85°; the *hydroxide* on decomposition gives dimethylaniline. *Phenyldiethylallylammonium*

iodide from ethylallylaniline and ethyl iodide, or from diethylaniline and allyl iodide; *platinichloride*, needles, m. p. 158—159°; the *hydroxide* on decomposition gives diethylaniline. Phenylmethyl-*n*-propylallylammonium iodide, prisms, m. p. 119—120°, from methyl-*n*-propylaniline and allyl iodide, or as a gummy mass from methylallylaniline and *n*-propyl iodide; *platinichloride*, needles, m. p. 157—158°; the *hydroxide* on decomposition gives *n*-propylallylaniline. Phenylmethyl*iso*butylallylammonium iodide from methyl*iso*butylaniline and allyl iodide, needles, m. p. 124°; *platinichloride*, needles, m. p. 156—157°; the *hydroxide* on decomposition yields *iso*butylallylaniline. Phenylmethyl*iso*amylallylammonium iodide, prisms, m. p. 126—127°, from methyl*iso*amylaniline and allyl iodide; *platinichloride*, needles, m. p. 154—155°; the hydroxide on decomposition gives *iso*amylallylaniline.

Phenylmethylethyl-n-*butylammonium iodide*, prisms, m. p. 72—73°, obtained from methylethylaniline and *n*-butyl iodide, also from ethyl-*n*-butylaniline and methyl iodide; *platinichloride*, needles, m. p. 195—196°, was obtained also from the gummy reaction product of methyl-*n*-butylaniline and ethyl iodide; the *hydroxide* on decomposition gives methyl-*n*-butylaniline. *Phenylmethylethyl*iso*amylammonium iodide*, needles, m. p. 154°, was obtained from ethyl*iso*amylaniline and methyl iodide, also from methylethylaniline and *iso*amyl iodide, and from methyl*iso*amylaniline and ethyl iodide; *platinichloride*, m. p. 191—192°; the *hydroxide* on decomposition gives methyl*iso*amylaniline.

Phenylmethyl-n-*propyl*iso*butylammonium iodide*, a viscous mass, from methyl*iso*butylaniline and *n*-propyl iodide, and also from methyl-*n*-propylaniline and *iso*butyl iodide; *platinichloride*, needles, m. p. 200—201°; the *hydroxide* on decomposition yields methyl-*n*-propylaniline.

Phenylmethyl-n-*propyl*iso*amylammonium iodide*, obtained as a gummy mass from methyl*iso*amylaniline and *n*-propyl iodide and also from methylpropylaniline and *iso*amyl iodide; platinichloride, needles, m. p. 183—183·5°; the hydroxide on decomposition gives methyl-*n*-propylaniline. *Phenylmethyl*-n-*butyl*iso*amylammonium iodide*, obtained as a gummy mass from methyl*iso*amylaniline and *n*-butyl iodide, and also from methyl-*n*-butylaniline and *iso*amyl iodide; *platinichloride*, needles, m. p. 191—192°; the hydroxide on decomposition gives methyl*iso*amylaniline.

D. F. T.

Esters Derived from Cyclanols and Acids of the Formic Acid Series. JEAN B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1912, 155, 1012—1014).—By a method previously described (A., 1912, i, 694) a series of esters has been prepared from *cyclo*hexanol and the three methyl *cyclo*hexanols and formic, acetic, propionic, butyric, *iso*butyric, and *iso*valeric acids. They are all colourless liquids with a pleasant odour, and are not affected by light, save the *o*-methyl*cyclo*hexyl esters, which turn slightly yellow on prolonged exposure. The following physical constants were determined. The b. p.'s are all at 750—753 mm.:

	*cyclo*Hexyl.		Methyl*cyclo*hexyl. Ortho.			Meta.			Para.		
	b. p.	D_4^0.	b. p.	D_4^0.	n_D^{18}.	b. p.	D_4^0.	n_D^{18}.	b. p.	D_4^0.	n_D^{18}.
Formate	162·5°	1·0057	173·0°	0·9813	—	176·5°	0·9775	—	177·5°	0·9761	—
Acetate	174·0	0·9854	184·5	0·9636	—	187·5	0·9592	—	188·5	0·9578	—
Propionate ...	193·0	0·9718	203·0	0·9548	1·444	206·0	0·9509	1·442	207·0	0·9492	[illegible]
Butyrate	212·0	0·9572	221·5	0·9443	1·445	224·5	0·9403	1·4435	225·5	0·9386	[illegible]
*iso*Butyrate...	204·0	0·9489	212·5	0·9364	1·441	215·0	0·9318	1·440	216·0	0·9304	[illegible]
*iso*Valerate...	223·0	0·9425	231·5	0·9316	1·444	234·0	0·9275	1·4425	235·0	0·9262	[illegible]

In passing up the acid series there is an increase of 18·5—19° in the b. p. from one homologue to the next higher, except in the case of the formates, whilst the densities decrease, but in an irregular manner.

W. G.

Esterification of Cyclanols by Aromatic Acids. JEAN B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1912, 155, 1254—1256).—Applying the method used for fatty acids (A., 1912, i, 694) to aromatic acids having the carboxyl group attached to the benzene nucleus, in no case was an ester obtained, but the *cyclo*hexanol was always converted into *cyclo*hexene. If, however, the carboxyl group is in the side-chain, condensation readily occurred, and the following esters were prepared:

cyclo*Hexyl phenylacetate*, b. p. 180·5°, D_4^0 1·0535, n_D^{13} 1·518.

cyclo*Hexyl phenylpropionate*, b. p. 193·5°, D_4^0 1·0432, n_D^{13} 1·515.

o-*Methyl*cyclo*hexyl phenylacetate*, b. p. 186°, D_4^0 1·0374, n_D^{13} 1·512; the meta-*isomeride*, b. p. 188°, D_4^0 1·0323, n_D^{13} 1·510; and the para-*isomeride*, b. p. 188·5°, D_4^0 1·0316, n_D^{13} 1·509.

o-*Methyl*cyclo*hexyl phenylpropionate*, b. p. 198·5°, D_4^0 1·0286, n_D^{13} 1·510; the meta-*isomeride*, b. p. 200°, D_4^0 1·0235, n_D^{13} 1·508; and the para-*isomeride*, b. p. 200·5°, D_4^0 1·0225, n_D^{13} 1·507.

Menthyl phenylacetate, an oily liquid, b. p. 205·5°/25 mm., D_4^{17} 0·9887.

Menthyl phenylpropionate, needles, m. p. 28·5°, b. p. 216°/25 mm.

W. G.

Action of Potassium Hydroxide on *cyclo*Hexanol; Synthesis of *cyclo*Hexyl*cyclo*hexanol and of Di*cyclo*hexyl*cyclo*hexanol. MARCEL GUERBET (*Compt. rend.*, 1912, 155, 1156—1159. Compare A., 1912, i, 67, 154).—*cyclo*Hexanol, like other secondary alcohols, undergoes condensation when heated at 230° with potassium hydroxide, some oxidation also occurring with the formation of potassium salts of acids. The following products were obtained by this method:

2-cyclo*Hexyl*-3-cyclo*hexanol*, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot C_6H_{11}\\ | \qquad\qquad\quad |\\ CH_2\cdot CH_2\cdot CH\cdot OH\end{matrix}$, a colourless, oily liquid, b. p. 178—180°/55 mm., D_4^0 0·9950, which yields an *acetate*, a colourless liquid with a pleasant odour, b. p. 188—190°/52 mm. On oxidation with chromic acid the alcohol is converted into 2-cyclo-

hexyl-3-cyclo*hexanone*, $C_6H_{11}\cdot C_6H_9O$, a colourless liquid, b. p. 176—178°/54 mm., yielding an *oxime*, m. p. 102°, and a *semicarbazone*, m. p. 149—150°.

A product of further condensation is 2-*dicyclohexyl*-3-cyclo*hexanol*, $\begin{matrix} CH_2\cdot CH_2\cdot CH\cdot C_6H_{10}\cdot C_6H_{11} \\ CH_2\cdot CH_2\cdot CH\cdot OH \end{matrix}$, prismatic crystals, m. p. 124°.

The acids obtained due to a secondary reaction are hexoic acid, b. p. 204—207°, and cyclo*hexyl*cyclo*hexanoic acid*, $C_6H_{11}\cdot C_6H_{11}O_2$ (?), a colourless, oily liquid, b. p. 218—220°/69 mm., D_4^0 1·010, yielding a *barium* salt, crystallising from alcohol. W. G.

Catalytic Action. V. Comparison of the Action of Various Catalysts III. Acetylation of *o* Nitrophenol, Carbazole, and Diphenylamine, and Some Observations on *o*-Nitroaniline and Tribromophenol as well as their Acyl Derivatives. JACOB BÖESEKEN (*Rec. trav. chim.*, 1912, **31**, 350—366. Compare A., 1911, i, 22).—Further acetylations have been studied in order to find a simple reaction on which quantitative researches on the influence of catalysts may be based. As a rule, the acetylation of primary amines is too complicated, for both mono- and di-acyl compounds are often produced; thus when *o*-nitroaniline is warmed for a quarter of an hour with acetic anhydride and a trace of sulphuric acid or aluminium chloride, the resulting diaceto-*o*-nitranilide contains a little of the mono-derivative.

The case of *s*.-tribromophenol has already been studied by Smith and Orton (T., 1909, **95**, 1063), but their method is criticised, for the acetic acid employed may have influenced the catalysts and their estimation of the final products does not seem to have been trustworthy, since the acetate is somewhat saponified on boiling with water. Titration of the alkali required to saponify the acetate is also found unsatisfactory. The solidification points of mixtures of tribromophenol (m. p. 92·5°) with the acetate (m. p. 82°) have therefore been plotted, but the curve is irregular, and indicates the formation of molecular compounds with m. p. about 65°.

In the case of *o*-nitrophenol, however, a simple solidification curve has been obtained, and found to provide the best means of estimating a mixture of the two compounds. The product of the reaction is washed with ice water, extracted with benzene, and the extract is dried and allowed to evaporate at 50°. By this means it is found that *o*-nitrophenol is acetylated by acetic anhydride at 98° to the extent of 92% in about four and a-half hours. Hydrogen chloride has only a feeble influence, for in one and a-half hours and with 50 molecules of the gas per 100, the process is only two-thirds complete, whereas 3 molecules per 100 of aluminium chloride complete the reaction in one and a-half hours, and 3 molecules per 100 of anhydrous ferric chloride do so in ten minutes.

Diphenylamine is so completely acetylated without catalytic agency on heating with acetic anhydride on the steam-bath that the present studies were carried out at 45°, again with the aid of a solidification curve. Fuming sulphuric acid, ferric chloride, aluminium chloride, and acetyl chloride have nearly equal effects, and the conclusion is drawn

that the catalysts have formed compounds with one of the systems already present, and that it is their influence that is being studied. The formation of sulphacetic acid and probably mono- and di-acetyl-sulphuric acids from acetic anhydride and sulphuric acid (Franchimont, A., 1881, 716) is of importance in this connexion, as well as the fact that aluminium chloride and acetic anhydride produce acetyl chloride (see this vol., i, 6).

Since carbazole is unaffected by alcoholic potash, it was found possible to analyse the mixture by titrating the alkali required for the saponification of the acyl derivative. Without a catalyst, scarcely any acetylation has taken place after five hours at 98°, but with a trace of sulphuric acid or with quite minute amounts of ferric chloride, the process is complete in half an hour. J. C. W.

Nitro-derivatives of Diphenylene Oxide and of Phenyl Ether. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1912, [iv], 11, 1011—1014).—An error in the calculation of nitrogen has led to the description of nitro-derivatives of phenyl ether containing more than four nitro-groups (Mailhe and Murat, A., 1912, i, 346), of penta- and hexa-nitrodiphenylene oxides, and of the disulphonic acid derivative of the latter (Mailhe, A., 1912, i, 553). These substances do not exist. H. W.

***m*-Dithiolbenzene (Dithioresorcinol).** THEODOR ZINCKE and OTTO KRÜGER (*Ber.*, 1912, **45**, 3468—3479).—The *m*-Dithiolbenzene was prepared in the ordinary way from benzene-1:3-disulphonyl chloride by reduction with zinc and hydrochloric acid. In order to obtain good yields the zinc sulphinate must first be formed by the action of the zinc on the chloride in alcoholic solution, and afterwards reduced to the mercaptan by the addition of hydrochloric acid and further action of the zinc. If this method of procedure is not adopted, the free sulphinic acid and the mercaptan react with the formation of tetra- or poly-sulphides.

The following derivatives of *m*-dithiolbenzene have been prepared. *Di-1:3-phenylene disulphide*, $S_2(C_6H_4)_2S_2$, prepared by the action of perhydrol in alkaline alcoholic solution, forms a yellowish-white, amorphous powder. 4:6-*Dichloro*-1:3-*dichlorothiolbenzene*,

$$C_6H_2Cl_2(SCl)_2,$$

is obtained by chlorination in chloroform solution. It may also be prepared from the benzyl ester. It forms yellow, glistening needles, m. p. 103°, and shows the usual reactions of the arylsulphur chlorides. When warmed with acetone, it gives slender, colourless needles of 4:6-*dichloro*-1:3-*diacetonylthiolbenzene*, $C_6H_2Cl_2(S\cdot CH_2Ac)_2$, m. p. 97°.

On methylation with methyl sulphate, *m*-dithiolbenzene gives 1:3 *dimethylthiolbenzene*, $C_6H_4(SMe)_2$, a strongly refracting liquid with characteristic odour, b. p. 149°/17 mm., which on treatment with 1:4-nitric acid in glacial acetic acid solution yields 4-*nitro*-1:3-*dimethylthiolbenzene*, $NO_2\cdot C_6H_3(SMe)_2$, yellow, glistening needles, m. p. 114°. The disulphoxide is formed at the same time. 1:3-*Diethylthiolbenzene*, $C_6H_4(SEt)_2$, is similar to the dimethyl ether, and has b. p.

164° 18—19 mm. 1 : 3-*Dibenzylthiolbenzene*, $C_6H_4(S\cdot CH_2Ph)_2$, crystallises in leaflets, m. p. 50°.

4 : 6-*Dichloro*-1 : 3-*dimethylthiolbenzene*, $C_6H_2Cl_2(SCH_3)_2$, prepared from the dimethyl ether by chlorination in glacial acetic acid solution, crystallises in long, glistening needles, m. p. 123°. When chlorination takes place in chloroform solution, 1 : 3-*ditrichloromethylthiolbenzene*, $C_6H_4(S\cdot CCl_3)_2$, is obtained as crystals, having the m. p. 106°. Under the action of aniline, fission occurs with the formation of dithiolbenzene and triphenylguanidine.

When the dimethyl ether is treated with bromine in chloroform solution, stout, dark orange needles of 4 : 6-*dibromo*-1 : 3-*dimethylthiolbenzene dibromide*, $C_6H_2Br_2(SMe)\cdot SBr_2Me$, are obtained. When shaken with sodium hydrogen sulphite solution in the presence of chloroform, 4 : 6-*dibromo*-1 : 3-*dimethylthiolbenzene* itself, $C_6H_2Br_2(SMe)_2$, is obtained as colourless, glistening needles, m. p. 142°. The same compound may be obtained from the disulphoxide by treatment with hydrogen bromide. 4 : 6-*Dibromo*-1 : 3-*diethylthiolbenzene tetrabromide*,

$$C_6H_2Br_2(SBr_2\cdot Et)_2,$$

results from the bromination of the diethyl ether in chloroform solution; it forms dark red, in reflected light steel-blue, needles, which readily lose bromine under the action of sodium hydrogen sulphite, giving 4 : 6-*dibromo*-1 : 3-*diethylthiolbenzene*, $C_6H_2Br_2(SEt)_2$, which crystallises in long, silky needles, m. p. 58°.

Oxidation of the dimethyl ether (1 part) with perhydrol (1·5 parts) in glacial acetic acid solution at the ordinary temperature gives white needles of *phenylene*-1 : 3-*dimethyldisulphoxide*, $C_6H_4(SOMe)_2$, m. p. 131°. The corresponding *disulphone*, $C_6H_4(SO_2Me)_2$, is obtained when 3 parts of perhydrol are used and the reaction completed on the water-bath; it crystallises in white, glistening leaflets, and has m. p. 196—197°. The following compounds were obtained in a similar manner: *Phenylene*-1 : 3-*diethyldisulphoxide*, $C_6H_4(SOEt)_2$, is a colourless, oily liquid; the *disulphone*, $C_6H_4(SO_2Et)_2$, forms colourless, clear plates, m. p. 142°. *Phenylene*-1 : 3-*dibenzyldisulphoxide*, $C_6H_4(SO\cdot CH_2Ph)_2$, gives colourless, glistening crystals, m. p. 131°, whilst the *disulphone*, $C_6H_4(SO_2\cdot CH_2Ph)_2$, forms tabular crystals, m. p. 229°. T. S. P.

4 : 4′-Dithioldiphenyl. THEODOR ZINCKE and ALEXANDER DAHM (*Ber.*, 1912, **45**, 3457—3468).—4 : 4′-Dithioldiphenyl was obtained from benzidine by Leuckart's method (A., 1890, 603), except that the decomposition of the diazoxanthate was carried out in the presence of copper powder, whereby explosions are avoided and better yields obtained. From this compound a number of derivatives have been obtained.

By the action of chlorine on the solution of the dimercaptan or of its benzyl ether in carbon tetrachloride, 4 : 4′-dichlorothioldiphenyl (A., 1911, i, 369) is obtained. This compound loses chlorine on warming with glacial acetic acid, alcohol or dilute alkali, giving a compound which is probably the tetrasulphide, $S_2(C_6H_4\cdot C_6H_4)_2S_2$. Oxidation with nitric acid or chlorine in glacial acetic acid solution gives the corresponding sulphonyl chloride. On heating with acetone, 4 : 4′-*diacetonylthioldiphenyl*, $C_{12}H_8(S\cdot CH_2Ac)_2$ is obtained in the form

of almost white needles, m. p. 165°. It can also be obtained from the dimercaptan and chloroacetone.

4:4'-Dimethylthioldiphenyl, $C_{12}H_8(SMe)_2$ (compare Leuckart, *loc. cit.*), is obtained by methylating the dimercaptan with methyl sulphate; m. p. 185°. The action of chlorine in glacial acetic acid solution gives the diphenyldichlorothiol, but in chloroform solution substitution occurs in the methyl groups, with the formation of 4:4'-*di-trichloromethylthioldiphenyl*, $C_{12}H_8(S{\cdot}CCl_3)_2$, white needles, m. p. 195°. When heated with aniline, triphenylguanidine and diphenyldithol are formed from the di-trichloro-compound.

4:4'-Diethylthioldiphenyl, $C_{12}H_8(SEt)_2$ (compare Leuckart, *loc. cit.*), is prepared similarly to the ethyl compound. The action of chlorine in chloroform solution gives a red oil. It forms a *tetrabromide* and *hexaiodide*.

4:4'-*Dibenzylthioldiphenyl*, $C_{12}H_8(S{\cdot}CH_2Ph)_2$, forms white, glistening, leaflets, m. p. 198—199°. Chlorination in chloroform solution gives benzylidene chloride and the dichlorothioldiphenyl.

4:4'-*Dimethylthioldiphenyl tetrabromide*, $C_{12}H_8(SMeBr_2)_2$, is obtained as a red, crystalline precipitate by the action of dry hydrogen bromide on the corresponding sulphoxide (see later) in chloroform solution; m. p. 130° (decomp.). Thiosulphate, sodium sulphite, or concentrated alkali eliminates bromine, whilst water or very dilute alkali regenerates the sulphoxide to some extent. The *hexabromide*, $C_{12}H_8(SMeBr_2)_2,Br_2$, prepared from the dimethyl ester by direct addition of bromine in chloroform solution, forms dark red crystals, and has m. p. 90° (decomp.). It behaves similarly to the tetrabromide towards bromine-eliminating agents. The *hexaiodide*, $C_{12}H_8(SMeI_2)_2,I_2$, is prepared similarly to the hexabromide, and has m. p. 198° (decomp.); it forms almost black crystals. It can also be obtained from the disulphoxide and hydrogen iodide. Iodine is eliminated by the usual agents, but the disulphoxide cannot be obtained from it.

4:4'-*Diphenyldimethyldisulphoxide*, $C_{12}H_8(SOMe)_2$, prepared from the dimethyl ether by oxidation with hydrogen peroxide or nitric acid (D 1·5), forms white leaflets, m. p. 195°. In glacial acetic acid solution it is reduced by hydrogen bromide or iodide, in contradistinction to its behaviour in chloroform solution (see above). Oxidation with perhydrol gives the *disulphone*, $C_{12}H_8(SO_2Me)_2$, white leaflets, m. p. 302°. The following sulphoxides and sulphones are prepared similarly: 4:4'-*Diphenyldiethyldisulphoxide*, $C_{12}H_8(SOEt)_2$, small, colourless needles, m. p. 134°; the *disulphone*, $C_{12}H_8(SO_2Et)_2$, forms white needles, m. p. 187°. 4:4'-*Diphenyldibenzyldisulphoxide*, $C_{12}H_8(SO{\cdot}CH_2Ph)_2$, consists of white needles, m. p. 243°, as also does the *disulphone*, $C_{12}H_8(SO_2{\cdot}CH_2Ph)_2$, m. p. 320°. T. S. P.

The Autoxidation of Trinaphthylcarbinol. JULIUS SCHMIDLIN and MAXIMILIAN BERGMAN (*Ber.*, 1912, 45, 3203—3205).—In reply to Tschitschibabin's criticism (A., 1911, i, 969) that of the two described isomerides of trinaphthylcarbinol (Schmidlin and Massini, A., 1909, i, 563) the more stable is in reality an oxidation product of the other, it is stated that this oxidation product (α-naphthyl-di-αα-naphthafluoryl alcohol) is a distinct substance, which causes a considerable depression

of the m. p. of the stable isomeride and is more easily obtained than the latter.

It has not hitherto been possible to prepare a triarylcarbinol containing only the diphenyl and naphthyl radicles; bis-diphenylyl ketone and also esters of diphenylcarboxylic acid refuse to react with magnesium naphthyl iodide, also dinaphthyl ketone with magnesium diphenyl bromide. D. F. T.

Preparation of Acetal Condensation Derivatives from Polyhydroxy-alcohols with Aldehydes or Ketones. WALTER GERHARDT (D.R.-P. 253083. Compare Harnitzky and Mentschutkin, *Annalen*, 1865, **136**, 126).—Glycerol benzylidene ether,

$$C_6H_5\cdot CH{<}^{O}_{O}{>}C_3H_5\cdot OH,$$

has now been obtained with b. p. 280° and m. p. 84° (compare Fischer, A., 1894, i, 395) by heating glycerol and benzaldehyde together at 135—145°.

The *compound*, $C_{10}H_{12}O_2$, b. p. 113·5—115·5°/14 mm., is obtained from propylene glycol and benzaldehyde at 162°; and the same aldehyde with trimethylene glycol furnishes *trimethylene glycol benzylidene ether*, $C_{12}H_{10}O_2$, m. p. 50°, b. p. 121—124°/15 mm.

Chlorohydrin benzylidene ether, $C_6H_5\cdot CH{:}O_2{:}C_3H_5Cl$, b. p. 144—146°/11 mm., is prepared from chlorohydrin and benzaldehyde; glycerol and anisaldehyde yield the *compound*, $C_{11}H_{14}O_4$, b. p. 208—210°/18·5 mm., whilst the *compound*, $C_{11}H_{12}O_5$, m. p. 107—107·5°, is furnished by glycerol and piperonal; and *acetophenone glycerol*, a viscous liquid, b. p. 156°/16 mm., is obtained from glycerol and acetophenone.

F. M. G. M.

Cubebin. IV. and V. EFISIO MAMELI (*Gazzetta*, 1912, **42**, ii, 546—550, 551—566. Compare A., 1908, i, 20; 1909, i, 503).—IV. *isoCubebin ether* is obtained when cubebin is dissolved in the least quantity of concentrated acetic acid and treated with a small quantity of concentrated sulphuric acid; on pouring the solution into water, the ether is precipitated. It forms colourless, acicular crystals, m. p. 157°, and has the composition and molecular weight required by the formula $C_{20}H_{18}O_5$. The substance is optically active, having $[\alpha]_D$ 26·02°. It reactions indicate that it is an internal ether.

Although cubebin ether is easily converted into cubebinol by reducing agents, *iso*cubebin ether resists such treatment, but it is converted into cubebinol when boiled with dilute acids.

V. This paper deals with hydroxycubebinic acid and some of its derivatives. The author has investigated the oxidation of cubebin and its derivatives by means of a large number of oxidising agents (hydrogen peroxide, bromine water, iodine water, Fehling's solution, silver oxide, Nessler's reagent, dilute nitric acid, lead nitrate, and lead peroxide, and hydrochloric acid), and has obtained in all cases results analogous to those previously obtained with other oxidising substances by himself and other observers. When, however, cubebin is suspended in strongly alkaline solution of sodium hypobromite at the ordinary temperature, a salt of a new acid, hydroxycubebinic acid, is produced.

The preparation is effected by keeping the reaction mixture in the dark for five or six days; the *sodium* salt which has separated (yield 93—96%) is collected and purified from admixed cubebin, which is insoluble in warm water. When the aqueous solution of this salt is treated with dilute sulphuric acid, the lactone, *cubebinolide*, $C_{20}H_{18}O_6$, is obtained; it forms colourless crystals, m. p. 63—64°, $[\alpha]_D$ +33·69° (in chloroform). This substance behaves in all its reactions as a lactone of a monocarboxylic acid. It dissolves with difficulty in boiling alkalis, yielding the sodium and *potassium* salts of hydroxycubebinic acid. The sodium salt, $C_{20}H_{19}O_7Na$, forms acicular crystals, which melt in their water of crystallisation at 70°; the anhydrous salt has m. p. 205—207°; the salt has no pharmacological action. The other salts were obtained from the sodium salt. The *strontium, magnesium, zinc, cadmium, iron, uranium, copper, cobalt, nickel, lead, manganese, calcium*, $Ca(C_{20}H_{19}O_7)_2$, and *barium*, $Ba(C_{20}H_{19}O_7)_2$, salts were prepared. Indications of the existence of the free acid were observed, but it was not possible to isolate it.

When cubebinolide is treated with magnesium phenyl bromide, a *diphenyl* derivative is obtained, which is to be regarded as the product of dehydration of the glycol which would be expected. This substance crystallises in colourless leaflets, m. p. 136—137°, $[\alpha]_D$ −178·78° (in chloroform), and has the probable formula $C_{32}H_{28}O_5$, although the analytical results do not agree with this very well.

When a methyl-alcoholic solution of cubebinolide is saturated with hydrogen chloride and kept in a sealed vessel, an *ester*, $C_{21}H_{21}O_6Cl$, is obtained; it crystallises in thin laminæ, m. p. 95°, $[\alpha]_D$ +13·89°. When saponified (with strong alkali) it yields a salt of hydroxycubebinic acid.

Oxidation of the lactone with dilute nitric acid gives a *dinitro*-derivative, m. p. 183—184°. The action of bromine on an alcoholic solution of the lactone yields a *dibromo*-derivative, m. p. 137°.

The author gives provisional formulæ to illustrate possible modes of origin of the compounds above described, and their bearing on the constitution of cubebin. R. V. S.

Hydrolysis of *o*-Acetoxybenzoates and the Preparation of Calcium *o*-Acetoxybenzoate. MICHAEL MÁTHÉ (*Chem. Zentr.*, 1912, ii, 431; from *Pharm. Post*, 1912, 45, 474—476, 481—483).—The calcium salt was prepared by suspending slaked lime in alcohol and adding *o*-acetoxybenzoic acid, when the salt separated as a coagulated mass, which was washed with alcohol and dried at 40—60°. The sodium salt decomposes in aqueous solution more quickly than the lithium salt, and the latter at first more slowly, but eventually more quickly, than the calcium salt. The lithium salt decomposes when kept in dry powder, and also the calcium salt, but the latter only to a slight extent. In water, all three salts form acetic acid and the corresponding salicylate. T. A. H.

The Action of Hydrochloric Acid and Potassium Hydroxide on the Lactam of Benzoyldehydracetic Acid. JOH. SCHÖTTLE and PAVEL IV. PETRENKO-KRITTSCHENKO (*Ber.*, 1912, 45, 3229—3231. Compare A., 1911, i, 1020; 1912, i, 128).—It has already been

observed that the action of concentrated hydrochloric acid and sodium hydroxide solutions on the lactam of benzoyldehydracetic acid produces 2 : 6-diphenyl-4-pyridone-3-carboxylic acid and 2 : 6-diphenyl-4-pyridone respectively.

The action of hydrochloric acid in dilute solution in aqueous alcohol, or of dilute solution of potassium hydroxide in alcohol, gives rise to benzoyldehydracetic acid. This easy removal of nitrogen from the ring does not militate against the structure assumed for the lactam, as the alternative possibility of the position of the nitrogen atom in the side-chain would necessitate the assumption that ammonium chloride (in the action of concentrated solution of acid or alkali) can condense with benzoyldehydracetic acid—an assumption which is not in accord with experimental evidence.

The amide of dehydracetic acid, when heated in a sealed tube with hydrochloric acid at 180°, quantitatively eliminates a molecule of ammonia. D. F. T.

Nitrogentisic Acids. ALFONS KLEMENC (*Monatsh.*, 1912, **33**, 1243—1254).—The stability of gentisic acid (2 : 5-dihydroxybenzoic acid) is so increased by esterification that it can be successfully nitrated, especially if the hydroxyl groups are previously acetylated.

The methyl ester of diacetylgentisic acid, m. p. 62—63·5°, obtained by acetylation of methyl gentisate or by the action of diazomethane on diacetylgentisic acid, when nitrated with fuming nitric acid (D 1·52) and subsequently hydrolysed produces 3-*nitrogentisic acid*, a yellow powder, m. p. 230° (decomp.); *ammonium* salt, brown; the *silver* salt, a yellow, crystalline powder, on treatment with methyl iodide produces the *methyl* ester, yellow needles, m. p. 158° (decomp.), which can also be obtained by direct esterification of the acid by a methyl-alcoholic solution of hydrogen chloride.

Methyl 2-hydroxy-5-methoxybenzoate (Graebe and Martz, A., 1905, i, 702), when nitrated in acetic acid solution with fuming nitric acid, yields *methyl 3-nitro-2-hydroxy-5-methoxybenzoate*, yellow needles (from methyl alcohol), which change to leaflets, m. p. 138—139°; the *potassium* salt, yellow needles, obtained by hydrolysis, on acidification gives 3-*nitro-2-hydroxy-5-methoxybenzoic acid*, yellow needles, m. p. 181°.

Diazomethane acting in ethereal solution converts 3-nitrogentisic acid, and also 3-nitro-2-hydroxy-5-methoxybenzoic acid, into the *methyl* ester (colourless needles, m. p. 71—72°) of 3-*nitro-2 : 5-dimethoxybenzoic acid* (yellow needles, m. p. 181—183°), the acid being obtainable by hydrolysis.

The three nitro-acids described above all give characteristic colours when dissolved in potassium hydroxide solution. D. F. T.

Preparation of Anthraquinonecarboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 250742).—Anthraquinonecarboxylic acids can be readily prepared by oxidising the corresponding methylanthraquinones with nitrous fumes (NO_2 or N_2O_3) at a high temperature in the presence of a suitable solvent, whilst some nitroanthraquinones can be converted by the action of chlorine into the

corresponding chloroanthraquinones with elimination of the nitro-group.

1-*Chloroanthraquinone-2-carboxylic acid*, yellow needles, is obtained when 1-chloro-2-methylanthraquinone (25 parts) dissolved in 200 parts of trichlorobenzene is treated at 160° with the gases generated from a mixture of arsenious and nitric acids; and the required 1-chloro-2-methylanthraquinone is prepared by treating 1-nitro-2-methylanthraquinone with chlorine at 180°.

1 : 4-*Dichloroanthraquinone-2-carboxylic acid*, citron-yellow needles, is obtained from 1 : 4-dichloro-2-methylanthraquinone, whilst 2-methylanthraquinone furnishes *anthraquinone-2-carboxylic acid*.

F. M. G. M.

Benzalacetoneoxalic Acid [Benzylideneacetylpyruvic Acid]. OTTO MUMM (*Ber.*, 1912, 45, 3236—3237).—The condensation product of pyruvic acid with benzaldehyde described by Mumm and Bergell (A., 1912, i, 936) as benzylideneacetylpyruvic acid is in reality the isomeric ketoacetylphenylparacone, $CH_3\cdot CO\cdot CH<\begin{matrix}CO\cdot CO\\ CHPh\end{matrix}>O$ (Ruhemann, T., 1906, 89, 1236).

It is also formed from ethyl pyruvate and benzaldehyde, either from the sodium salt of the ester or from the free ester in presence of piperidine.

E. F. A.

The Combination of Phenolcarboxylic Acids. FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], 86, 550—551).—A correction. The products obtained by hydrolysing the compounds described in previous communications (A., 1911, i, 725; 1912, i, 267) with alkalis fully confirms the constitutions there given, and, therefore, the author retracts the statements made in his last paper (A., 1912, i, 858).

F. B.

Isomeric and Tautomeric Organo-magnesium Compounds. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÚS (*Ber.*, 1912, 45, 3193—3203).—The earlier explanation of the different behaviour of aromatic aldehydes with ordinary and previously heated solutions of magnesium triphenylmethyl chloride (Schmidlin, A., 1906, i, 392; 1907, i, 26, 601; 1908, i, 239) is adhered to in spite of the criticism of Tschitschibabin (A., 1909, i, 778). In refutation of the latter's criticism, it is stated that his experiments were not of a nature to decide the question, and it is further shown that, although magnesium benzyl chloride cannot be separated into two isomerides, the solution behaves as if it contained a tautomeric mixture of two isomerides, which, it is suggested, represent the normal and quinonoid configurations already assumed for the two forms of magnesium triphenylmethyl chloride.

When magnesium benzyl chloride solution in ether is treated with benzaldehyde, the latter being added in drops, the product is $\alpha\beta$-diphenylethyl alcohol, $CH_2Ph\cdot CHPh\cdot OH$. During the progress of the reaction, the Grignard reagent, which is believed to be an equilibrium mixture of the forms $CH_2{:}C_6H_4<\begin{matrix}H\\ MgCl\end{matrix}$ and $CH_2Ph\cdot MgCl$,

has time to rearrange so as to give a theoretical yield of the diphenylethyl alcohol produced by the latter form. If, however, the Grignard reagent is gradually introduced into the ethereal solution of benzaldehyde, both forms enter into reaction, and the product is a mixture of the above diphenylethyl alcohol with 1 : 3-*diphenyl-3 : 4-dihydro-2 : 1-benzopyran* (*diphenylisochroman*),

$$C_6H_4<\begin{matrix}CHPh\cdot O \\ CH_2—CHPh\end{matrix},$$

prismatic needles, m. p. 111·5° (corr.), b. p. 237°/9 mm., which dissolve in concentrated sulphuric acid to a green solution; on oxidation with potassium permanganate it gives *o*-benzoylbenzoic acid and benzoic acid, whilst chromic acid produces anthraquinone and benzoic acid. In the preparation of the above diphenyldihydrobenzopyran, there was occasionally obtained 1 : 3-*diphenyl-2 : 1-benzopyran* (*diphenyliso-chromene*), $C_6H_4<\begin{matrix}CHPh\cdot O \\ CH=\!=CPh\end{matrix}$, colourless needles, m. p. 125—126° (corr.); this decolorises bromine and potassium permanganate solutions, and gives a colourless solution in sulphuric acid; chromic acid gives the same oxidation products as with the dihydro-compound, whilst reduction by hydrogen and platinum-black produces the dihydro-derivative.

With other reagents, the magnesium benzyl chloride undergoes reaction merely through one of its isomerides; thus the action of carbon dioxide affects only the normal compound, whereas the formation of *o*-tolyl alcohol from formaldehyde (Tiffeneau and Delange, A., 1904, i, 48) depends on the reaction taking place with the quinonoid isomeride. D. F. T.

The Action of Ultraviolet Light on *o*-, *m*-, and *p*-Nitrobenzaldehyde and on Benzaldehyde. ANTON KAILAN (*Monatsh.*, 1912, 33, 1305—1327).—Under the action of ultraviolet light, *o*-nitrobenzaldehyde, both in alcoholic and benzene solutions, is slowly transformed into *o*-nitrosobenzoic acid (compare Ciamician and Silber, A., 1901, i, 547), the reaction taking place quicker in quartz than in glass vessels. The formation of acid from benzaldehyde takes place similarly. With both aldehydes the acid formation takes place more rapidly in benzene than in alcoholic solutions. The velocity of reaction increases with increase in concentration of the aldehyde, but proportionality does not exist, the increase in velocity being less than would be expected. Under similar conditions the amount of acid formed from the *o*-nitrobenzaldehyde is about twice as great as from the benzaldehyde. When the distance between the source of ultraviolet light (a mercury lamp) and the reaction vessel is increased, the diminution in reaction velocity is greater than would be expected from the inverse-square law. During the reaction a very considerable portion of the active rays is absorbed.

m- and *p*-Nitrobenzaldehydes, either as the solids or in solution, are hardly affected by ultraviolet light, the formation of acid being extremely small. Both solid *o*-nitrobenzaldehyde and liquid benzaldehyde are acted on to a considerable extent, in one case 87% of the benzaldehyde being converted into benzoic acid.

The formation of acid is due principally to oxidation by the oxygen of the air, or by ozone formed by the ultraviolet light; the reaction expressed by the equation: $2Ph\cdot COH + H_2O = Ph\cdot CH_2OH + Ph\cdot CO_2H$, if it takes place at all, plays only a subsidiary part.

In absolute alcoholic solution benzoic acid is not esterified to any appreciable extent under the conditions of experiment, nor does it have any accelerating action on the oxidation of the benzaldehyde, although hydrions, when present in great concentration, may exert such an action.

The temperature-coefficient of the above reactions is very small, as is usually the case in photochemical actions. T. S. P.

New Synthesis of *o*-Aldehydophenylnitrosohydroxylamine. OSKAR BAUDISCH (*Ber.*, 1912, 45, 3429—3430).—A solution of *o*-nitrobenzaldehyde in 96% alcohol (10 vol.) is diluted with 5 vol. of water, treated with 3 vol. of amyl nitrite and 3 vol. of concentrated aqueous ammonia, and then gradually with zinc dust. The reaction is complete after about fifteen minutes. The mixture is treated with an excess of aqueous copper sulphate, and dilute hydrochloric acid is added carefully with cooling. From the still alkaline solution is obtained a brown, flocculent precipitate, which is removed. The filtrate is rendered distinctly acid, whereby the copper derivative of *o*-aldehydophenylnitrosohydroxylamine is precipitated. After being washed with acetone, the copper salt is converted by aqueous alcoholic potassium hydroxide into the potassium salt, from which *o*-aldehydophenylnitrosohydroxylamine, m. p. 52·5°, is liberated by metaphosphoric acid. C. S.

Chemical Action of Light. II. Photo-Oxidation of the Aldehyde Group. I. Terephthalaldehyde. HERMANN SUIDA (*Monatsh.*, 1912, 33, 1173—1187. Compare A., 1912, i, 117).—Although terephthalaldehyde is very stable in the solid state and in solution in benzene in the dark, its solution undergoes rapid atmospheric oxidation when illuminated by a mercury lamp, and a white, crystalline deposit is formed; the deposit consists of terephthalaldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid; the solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution. This oxidation of terephthalaldehyde appears not to occur at all if light is excluded, and it is not accelerated by the presence of nitrobenzene, this substance, indeed, exerting a hindering effect; a comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthaldehyde is considerably diminished by the presence of a similar group in the para-position. By interposing solutions of potassium chromate and of quinine sulphate between the solution and the source of light, it is discovered that the effect is mainly due to the ultra-violet rays, but that yellow and red light can cause the oxidation to occur, although only very feebly. Spectrographic examination indicates that the effective rays are from 400 to 300$\mu\mu$. D. F. T.

Catalytic Reduction. VII. The Preparation and Application of Colloidal Platinum Metals. Aladar Skita and W. A. Meyer (*Ber.*, 1912, **45**, 3579—3589).—When submitted to the action of free hydrogen, an aqueous alcoholic solution containing an unsaturated aldehyde or ketone with a little palladious chloride and gum arabic undergoes reduction; colloidal palladium is first formed, which then catalytically accelerates the hydrogenation of the ethylenic linking (Skita, A., 1909, i, 479). If the ethylenic substance does not contain a ketonic or aldehydic group, colloidal palladium is not obtained, but precipitated metal, which, however, is sufficient to aid the reduction of camphene to dihydrocamphene, and of β-phenylvinyl acetate to *β-phenylethyl acetate*, b. p. 109—112°/13 mm., although it fails to reduce double bonds in aromatic nuclei. This action of the carbonyl group in aiding the formation of colloidal palladium is probably due to the formation of a double compound of the ketone or aldehyde with the greater portion of the metallic chloride present (compare Zeisse, *Annalen*, 1840, **33**, 29); under such conditions it is probable that colloidal particles are first formed which can cause the separation of the rest of the metal in the same form. This is confirmed by the behaviour at the ordinary temperature of a solution of palladious chloride and gum arabic, which, after the addition of a little colloidal palladium, is rapidly reduced by hydrogen to the colloidal metal, whereas if treated directly with hydrogen the metal is slowly precipitated in an insoluble form; this effect is not merely due to the prevention of supersaturation (Zsigmondy, A., 1906, ii, 679), but is also in part catalytic.

A colloidal solution of palladium can also be obtained by the action of hydrogen on a hot aqueous solution of palladious chloride containing gum arabic; when a mixture of this solution with an alcoholic feebly acid solution of piperine was treated with hydrogen, tetrahydropiperine (Skita and Franck, A., 1911, i, 1017) was produced.

Solutions of palladious chloride and of potassium platinosochloride containing gum arabic, when treated with sodium carbonate, give palladious and platinous hydroxides in a colloidal condition; careful evaporation in a vacuum, after dialysis, gives a residue of brown palladious hydroxide or black platinous hydroxide consisting of scales, which readily dissolve in water again. These colloidal hydroxides are well suited to reduction processes, for example, hydrogen reduced an aqueous alcoholic solution of pinene containing a little palladium hydroxide to pinane, and a solution of phorone containing a little platinum hydroxide readily absorbed an amount of hydrogen corresponding with two ethylenic linkings.

Colloidal palladium hydroxide solutions when shaken with hydrogen are reduced to colloidal palladium, and on evaporation in a vacuum black scales are obtained which readily re-dissolve in water; black scales of colloidal platinum can be similarly obtained. These, which can also be prepared directly by reduction of the corresponding chlorides, are again suitable for reduction experiments, *o*-nitroacetophenone and nitrobenzene being easily reduced to the corresponding amino-compounds.

The most satisfactory method for the hydrogenation of an un-

saturated compound is to add to the solution of platinum chloride and gum arabic a trace of a colloidal palladium or platinum solution, and then to act with hydrogen; the unsaturated substance which may be present from the commencement or introduced later is then easily reduced, for example, quinine yields dihydroquinine, whilst diacetylmorphine gives *diacetyldihydromorphine*, needles, m. p. 158° (*hydrochloride*, needles, m. p. above 300°), and cinnamic acid yields β-phenylpropionic acid. D. F. T.

Catalytic Reduction. VIII. Hydrogenation of Aldehydes and Ketones, and of Aromatic and Heterocyclic Substances in Colloidal Solutions. ALADAR SKITA and W. A. MEYER (*Ber.*, 1912, **45**, 3589—3595. Compare preceding abstract).—It has already been observed that hydrogenation occurs more readily in certain solvents than in others (Fokin, A., 1907, i, 819), and that acetic acid is so suitable that in the presence of platinum black even aromatic substances can be reduced (Willstätter and Hatt, A., 1912, i, 545). By using a colloidal solution of platinum, prepared by one of the methods described (preceding abstract), and applying acetic acid as solvent, it is found possible with hydrogen under an additional pressure of one atmosphere, to reduce toluene to methyl*cyclo*hexane, benzoic acid to *cyclo*hexanecarboxylic acid, naphthalene to decahydronaphthalene, pyridine to piperidine, heptaldehyde to heptyl alcohol, dihydro*iso*phorone to *trans*-dihydro*iso*phorol, and benzene to *cyclo*hexane; in the last two cases only a trace of colloidal platinum was taken with a solution of the substance for reduction, together with chloroplatinic acid, so that the treatment with hydrogen first produced the catalyst, and then reduced the organic substance; the reduction processes generally occupied one to three hours. Quinoline, however, required longer treatment with a rather higher pressure of hydrogen for reduction to decahydroquinoline, and by checking the reduction at the right stage, tetrahydroquinoline could be obtained. A description of the apparatus employed is given.

It was not found possible to replace gum arabic satisfactorily by any other protecting colloid. D. F. T.

Condensation Products of Cyclic Ketones with Acetone. OTTO WALLACH and W. VON RECHENBERG (*Chem. Zentr.*, 1912, ii, 923—924; from *Nachr. K. Ges. Wiss. Gött.*, 1912, 442—445).—Further investigation of the condensation of acetone with 1 : 3-methyl*cyclo*hexanone (A., 1896, i, 572; 1897, i, 425) shows that condensation takes place between the O-atom of the cyclic ketone and hydrogen from the acetone, with the production of compounds having a :CO group in the side-chain, which can be reduced to saturated ketones of the type $R\cdot CH_2\cdot COMe$, where R is a cyclic radicle. The position of the ethylenic linking is uncertain, but it is probably cyclic.

1:3-*Methyl*cyclo*hexylacetone*, b. p. 211·5—212°, $D^{21\cdot5}$ 0·8915, $n_D^{21\cdot5}$ 1·4496, obtained by reducing the methyl*cyclo*hexenylacetone produced by condensing 1-methyl*cyclo*hexan-3-one with acetone (*loc. cit.*), is lævorotatory, resembles other extra-cyclic ketones in aroma, gives a *semi-*

carbazone, m. p. 154°, and on oxidation with sodium hypobromite yields 1 : 3-methyl*cyclo*hexylacetic acid. 1 : 4-*Methyl*cyclo*hexenylacetone*, b. p. 216—217°, D^{21} 0·916, n_D^{21} 1·4672, has an anise odour, gives a *semicarbazone*, m. p. 122—123°, and a liquid *oxime*. On reduction it yields 1 : 4-*methyl*cyclo*hexylacetone*, b. p. 214—215°, D^{21} 0·8930, n_D^{21} 1·4499. The latter gives a *semicarbazone*, m. p. 166°, and is oxidised by sodium hypobromite to 1 : 4-methyl*cyclo*hexylacetic acid. T. A. H.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. II. Pieter J. Montagne and Jacob Moll van Charante (*Rec. trav. chim.*, 1912, 31, 298—349. Compare A., 1908, i, 988).—The action of alcoholic potash on further derivatives of benzophenone is described. It is found that the introduction of an amino-group into any position in the ring entirely prevents the reduction to a benzhydrol, but that the presence of methyl, chlorine, or bromine in the *para*-position, or of chlorine in the *ortho*-position, is without influence on the reduction. In the case of the bromo-derivatives it was previously found that 2 : 4 : 6-tribromobenzophenone is not only reduced, but that it also loses the bromine atoms in 2 and 6 (A., 1910, i, 42). Studying this detaching influence of the –COPh group further, it is found that the elimination of bromine occurs readily in the case of *o*-bromobenzophenone, to a slight extent with the para-compound, and to a still smaller extent, but certainly, with the meta-derivative. The –CHPh·OH group, on the contrary, has no such detaching influence, the substituted benzhydrols remaining entirely unchanged when heated with alcoholic potash; only in the case of the 4 : 4′-dibromobenzhydrol was there any trace of halogen removed. The following benzophenones have been studied: 2-, 3-, and 4-chloro-, 4 : 4′-dichloro-, 2-, 3-, and 4-bromo-, 2 : 4-, 2 : 6-, and 4 : 4′-dibromo-, 4-iodo-, 2-amino-, 2 : 2′-diamino-, 4 : 4′-didimethylamino- (Michler's ketone), 2- and 3-methyl-. Many of these have been described by Montagne and Koopal (see Koopal, Thesis).

2 : 4-Dibromobenzophenone was obtained by the action of benzoyl chloride and aluminium chloride on 1 : 3-dibromobenzene (Boeseken, A., 1908, i, 189) and also synthesised as follows: Acetanilide was converted into 2 : 4-dibromoacetanilide, not by Chattaway's method (A., 1900, i, 152), since that yielded only *p*-bromoacetanilide, but according to Mannino and Donato (A., 1908, i, 826). This was saponified by 10% potassium hydroxide, and the 2 : 4-dibromoaniline diazotised. With amyl nitrite, nitrous acid, or sodium nitrite and dilute sulphuric acid, a varying quantity of 2 : 4 : 2′ : 4′-tetrabromodiazoaminobenzene crystallised out, but on warming with water the mixture gave a good yield of 1 : 3-dibromobenzene. When mixed with potassium nitrite and added to concentrated nitric acid, the formation of a diazoamino-compound was prevented (compare O. N. Witt, A., 1909, i, 855), and on warming the diluted diazotised liquid with a mixture of copper sulphate and potassium cyanide the 2 : 4-dibromobenzonitrile was obtained. This was saponified and the acid converted into the chloride, which with benzene and aluminium chloride gave the 2 : 4-dibromobenzophenone. From the mother liquors of this compound a small amount of 2 : 6-dibromobenzo-

phenone was recovered, the two bromine atoms exerting no steric hindrance, which confirms the author's experience that the Friedel and Crafts's reaction on halogenated benzenes gives rise to ortho- as well as to para-substitution.

2 : 6-Dibromobenzophenone was also synthesised. Sulphanilic acid was converted into dibromoaniline (Orton and Pearson, T., 1908, 93, 735), and this was diazotised as above and converted into 2 : 6-dibromobenzonitrile, which was saponified by 65% sulphuric acid. The amide, m. p. 208·5°, was further treated with 90% sulphuric acid, and the 2 : 6-dibromobenzoic acid was converted into 2 : 6-dibromobenzoyl chloride and this into 2 : 6-*dibromobenzophenone*, $C_6H_3Br_2$·COPh, which crystallises in very long needles, m. p. 121·5°, b. p. 381°.

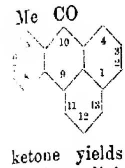
4-Aminobenzophenone, m. p. 124°, obtained by the reduction of 4-nitrobenzophenone (Shröter, A., 1909, i, 773) was found to remain unchanged by acetic acid, and was thus distinguished from 4-aminobenzhydrol, m. p. 121°, since the latter gives an acetyl compound, m. p. 153° (Doebner, A., 1882, 507). New benzhydrols obtained by the action of alcoholic potash on the benzophenones are 3-*bromobenzhydrol*, C_6H_4Br·CHPh·OH, m. p. 43°, and 3-*methylbenzhydrol*, C_6H_4Me·CHPh·OH, slender needles, m. p. 53°.

Detailed crystallographic measurements of the following substances have been made: 4-bromoacetanilide, 2 : 4-dibromoacetanilide, 2 : 4-dibromoaniline, 2 : 4-dibromobenzophenone, 2 : 6-dibromobenzamide, and 2-nitrobenzophenone. J. C. W.

Conversion of Distyryl Ketone into 2 : 6-Diphenylpyrone. DANIEL VORLÄNDER and G. A. MEYER (*Ber.*, 1912, **45**, 3355—3358).—Distyryl ketone tetrabromide (Claisen and Claparède, A., 1882, 511) when heated in alcoholic solution with a quadrimolecular quantity of potassium hydroxide is converted into a viscous oil, probably the diethoxy-compound, CO(CH:CPh·OEt); the substance gives a blood-red solution in sulphuric acid and a gradual brownish-black coloration with ferric chloride solution. When it is heated with hydrochloric acid (D 1·1) under reflux condenser for several hours a mixture of 2 : 6-diphenylpyrone, needles, m. p. 139—140°, with much resinous matter is produced. D. F. T.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. ROLAND SCHOLL and CHRISTIAN SEER (*Annalen*, 1912, **394**, 111—177).—Isolated instances of the union of aromatic nuclei by means of aluminium chloride at elevated temperatures are known, for example, the formation of perylene from 1 : 1'-dinaphthyl (Scholl, Seer, and Weitzenböck, A., 1910, i, 616), of flavanthrene from 2-aminoanthraquinone (Scholl, A., 1907, i, 540), and of *meso*-naphthadianthrone from *meso*-benzdianthrone (Scholl and Mansfeld, A., 1910, i, 494). The authors have now examined this reaction more fully, and find that, by means of anhydrous aluminium chloride at 80—140°, aromatic nuclei can be very satisfactorily united, particularly in the case of aromatic

ketones, where the elimination of the hydrogen is accompanied by the formation of new rings; thus, 1:9-benzanthrone is obtained in 76% yield by heating phenyl α-naphthyl ketone and anhydrous aluminium chloride (5 pts.) at 150° during two and a-half hours. In a similar manner, *o*-tolyl α-naphthyl ketone yields 5-*methyl*-1:9-*benzanthrone* (annexed formula), m. p. 167—168°, yellow needles; *m*-tolyl α-naphthyl ketone yields 6-*methyl*-1:9-*benzanthrone*, m. p. 169·5°, yellow needles; *p* tolyl α-naphthyl ketone yields 7-*methyl*-1:9-*benzanthrone*, m. p. 158—159°, yellow needles; *p*-diphenylyl α-naphthyl ketone yields 7-*phenyl*-1:9-*benzanthrone*, m. p. 170—171°, yellowish-brown leaflets; phenyl α-4-hydroxynaphthyl ketone yields 2-*hydroxy*-1:9-*benzanthrone*, m. p. 304°, dark red needles (*benzoyl* derivative, m. p. 236°, golden-yellow needles). In the last preparation, 2-*hydroxydihydro*-1:9-*benzanthrone*, m. p. 142—143°, yellowish-brown needles, is first formed; it is converted into 2-hydroxy-1:9-benzanthrone by prolonged heating or by passing oxygen through its solution in hot aqueous sodium hydroxide.



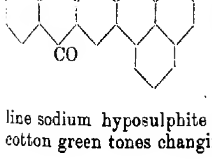
The interaction of naphthalene, *o*-toluoyl chloride, and aluminium chloride in carbon disulphide leads to the formation of o-*tolyl* α-*naphthyl ketone*, $C_{10}H_7{\cdot}CO{\cdot}C_6H_4Me$, m. p. 64°, b. p. 365—375°. By similar methods, m-*tolyl* α-*naphthyl ketone*, m. p. 74—75°, and p-*tolyl* α-*naphthyl ketone*, m. p. 85°, have been prepared. p-*Diphenylyl* α-*naphthyl ketone*, $C_{10}H_7{\cdot}CO{\cdot}C_6H_4Ph$, m. p. 136—137°, is obtained in a similar manner from α-naphthoyl chloride and diphenyl, or from naphthalene and the *chloride*, m. p. 114—115°, colourless needles, of diphenyl-4-carboxylic acid. *Phenyl* α-4-*hydroxynaphthyl ketone*, $OH{\cdot}C_{10}H_6{\cdot}COPh$, m. p. 164—165°, is obtained from α-naphthol and benzoyl chloride by Doebner's method.

o-α-Naphthoylbenzoic acid yields naphthanthraquinone, not the expected 1:9-benzanthrone-5-carboxylic acid, by heating with aluminium chloride.

[With Otto von Seybel.]—The interaction of the chloride of anthraquinone-2-carboxylic acid, naphthalene, and aluminium chloride in nitrobenzene at 75—80° for ten hours leads to the formation of a mixture of α-*naphthyl* 2-*anthraquinonyl ketone*,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_3{\cdot}CO{\cdot}C_{10}H_7,$$

m. p. 166—166·5°, light brown leaflets, and the β-*isomeride*, m. p. 176—177°, citron-yellow needles, which is separated by repeated crystallisation from glacial acetic acid and from pyridine. By heating with aluminium chloride at 100—140° for one hour and again at 140—145° for another hour, the former yields 6:7-*phthaloyl*-1:9-*benzanthrone* (annexed formula), m. p. 325—326°, dark yellow needles, which, unlike the α-naphthyl anthraquinonyl ketone, forms with alkaline sodium hyposulphite a dark green vat producing on unmordanted cotton green tones changing to yellow in air. The constitution of the



phthaloylbenzanthrone is proved by oxidation with chromic acid, whereby 2 : 3-*phthaloylanthraquinone-5-carboxylic acid*,

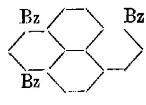
$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2{<}{}^{CO}_{CO}{>}C_6H_3{\cdot}CO_2H,$$

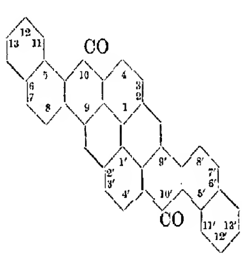
m. p. 338° (decomp.), microcrystalline, yellow needles, is obtained, which is converted by sublimation into Philippi's 2 : 3-phthaloylanthraquinone (A., 1911, i, 793). Phthaloylanthraquinonecarboxylic acid forms a greenish-yellow *sodium* salt, which forms with hot alkaline sodium hyposulphite a violet, and finally an orange, solution, changing to blue in air; this solution produces on unmordanted cotton a blue colour which becomes red by treatment with acids.

The interaction of pyrene, benzoyl chloride (rather more than 1 mol.), and aluminium chloride in carbon disulphide for twelve hours at the ordinary temperature, and then for an equal period on the water-bath, leads to the formation of 3-*benzoylpyrene*, m. p. 124—125°, yellow crystals, which is purified by means of the *picrate*, $C_{29}H_{17}O_8N_3$, m. p. 157°, orange needles. By using two or more mols. of benzoyl chloride, a mixture of di- and tri-benzoylpyrene is obtained, which is separated readily owing to the slight solubility of the latter in glacial acetic acid. 3 : 5 : 8-*Tribenzoylpyrene* (annexed formula), m. p. 239—240°, crystallises in yellow needles. 3 : 8-*Dibenzoylpyrene*, m. p. 158—160°, slender, yellow needles, yields pyrenequinone by oxidation with aqueous potassium dichromate and sulphuric and acetic acids, and is converted into pyranthrone when mixed with aluminium chloride, placed in a bath previously heated to 155—160°, and kept there for one hour (if the heating is effected gradually, the benzoyl groups are eliminated before the benzanthrone rings are formed). This formation of pyranthrone establishes the direct relation of the substance to pyrene, and also proves the orientation of the benzoyl groups in the dibenzoylpyrene. 3 : 5 : 8-Tribenzoylpyrene is converted into 3-*benzoylpyranthrone*, reddish-brown, metallic needles, in a similar manner; at a slightly higher temperature, 165—170°, the benzoyl group is eliminated and pyranthrone is formed. The interaction of pyrene, α-naphthoyl chloride, and aluminium chloride in carbon disulphide leads to the formation of a nearly quantitative yield of a mixture of 3 : 8- and 3 : 10-di-α-naphthoylpyrene, which is separated by boiling glacial acetic acid, in which the former is insoluble. 3 : 8-*Di-α-naphthoylpyrene*,

$$C_{38}H_{22}O_2,$$

m. p. 271·5—273°, crystallises in microscopic, yellow leaflets; the 3 : 10-*isomeride*, m. p. 219—220°, in yellow leaflets. The former and aluminium chloride at 140° for forty minutes yield 5 : 6 : 5′ : 6′-*dibenzpyranthrone* (annexed formula), a brown powder, which forms in hot alkaline sodium hyposulphite a sparingly soluble vat, by which unmordanted cotton is dyed blue, changing to orange-

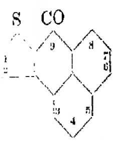




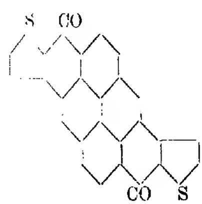
red in air. In a similar manner, pyrene, β-naphthoyl chloride, and aluminium chloride yield 3 : 10-*di-β-naphthoylpyrene*, m. p. 195·5—197°, yellow crystals (purified by means of the orange-yellow *picrate*), and 3 : 8-*di-β-naphthoylpyrene*, m. p. 289°, flattened, yellow needles. The latter and aluminium chloride at 145—155° yield 7 : 8 : 7′ : 8′-*dibenzpyranthrone*, a brown, indistinctly crystalline powder with green shimmer, which forms a vat behaving like that of the preceding isomeride.

It will be noticed that the action of the preceding acyl chlorides on pyrene in the presence of aluminium chloride yields in each case a pair of diacylpyrenes. One of these is undoubtedly the 3 : 8-diacylpyrene, since it is converted into benz-(or dibenz-)pyranthrone by aluminium chloride. It is known that hydrocarbons such as anthracene and phenanthrene, which are easily oxidised to quinones, are attacked in the Friedel-Crafts reaction by the acid chloride or anhydride in the same positions as by the oxidising agent in the formation of the quinone. Consequently it is probable that pyrene, which forms 3 : 8-diacylpyrenes in the Friedel-Crafts reaction, yields 3 : 8-pyrenequinone, not 3 : 10-pyrenequinone (Goldschmiedt, A., 1907, i, 310), by oxidation.

The constitution of violanthrone (Bally's violanthrene, A., 1905, i, 237) has been proved by the formation of the substance from 4 : 4′-dibenzoyl-$\alpha\alpha$-dinaphthyl and aluminium chloride at 95—100°.



The interaction of naphthalene, pyromucyl chloride, and aluminium chloride in carbon disulphide leads to the formation of (impure) *α-furyl α-naphthyl ketone*, $C_4OH_3·CO·C_{10}H_7$, b. p. 360—365°, which reacts with aluminium chloride to form a brown substance from which individual products have not been isolated. In a similar manner, naphthalene and the chloride of thiophen-2-carboxylic acid, or thiophen and α-naphthoyl chloride, yield *α-thienyl α-naphthyl ketone*, $C_4SH_3·CO·C_{10}H_7$, m. p. 68—69°, b. p. 383°, almost colourless needles, which is converted by aluminium chloride at 140—144° into *benzthiophanthrone*-9 (annexed formula), a brown, crystalline powder; this sinters at 210°, but is not fused at 250°, and yields by fusion with alcoholic potassium hydroxide a dye which is probably the analogue, $C_{30}H_{12}O_2S_2$, of violanthrone.

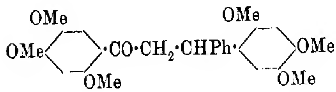


The interaction of pyrene, the chloride of thiophen-2-carboxylic acid, and aluminium chloride in carbon disulphide leads to the formation of 3 : 8-*di-α-thiophenoylpyrene*, $C_{26}H_{14}O_2S_2$, m. p. 278—279°, elongated, yellow leaflets, and 3 : 10-*di-α-thiophenoylpyrene*, m. p. 191—192°, yellow leaflets; the former and aluminium chloride at 150—158° yield *pyrthiophanthrone* (annexed formula), microscopic, reddish-brown needles. C. S.

Chalkones and Hydrochalkones. II. Guido Bargellini and Mina Finkelstein (*Gazzetta*, 1912, **42**, ii, 417—426. Compare Bargellini and Bini, A., 1912, i, 118).—The present paper describes

the reduction of four chalkones to the corresponding hydrochalkones by means of hydrogen in the presence of platinum black or palladium black.

2′ : 4′ : 5′-Trimethoxychalkone (compare Bargellini and Avrutin, A., 1911, i, 68) is conveniently prepared by the original method of preparation of chalkones (Stockhausen and Gattermann, A., 1893, i, 163). If, however, the heating of the mixture of hydroxyquinol trimethyl ether, cinnamyl chloride, and aluminium chloride is prolonged to ten or twelve hours, the principal product is a *substance*, $C_{27}H_{30}O_7$, which forms colourless needles, m. p. 127—128°. This compound dissolves in concentrated sulphuric acid, giving a pale yellow coloration, and does not react with bromine; it probably has the annexed constitution.



2′ : 4′ : 5′-*Trimethoxyhydrochalkone*, $C_{18}H_{20}O_4$, crystallises in colourless needles, m. p. 105—107°; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

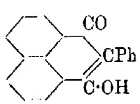
3 : 4 : 2′ : 4′ : 5′-*Pentamethoxyhydrochalkone*, $C_{20}H_{24}O_6$, forms colourless needles, m. p. 115—117°; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

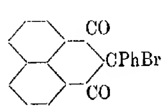
2′-*Hydroxy*-4 : 4′-*dimethoxyhydrochalkone*, $C_{17}H_{18}O_4$, crystallises in colourless needles, m. p. 58—60°.

2′-*Hydroxy*-3 : 4 : 4′-*trimethoxyhydrochalkone*, $C_{18}H_{20}O_5$, crystallises in colourless needles, m. p. 78—79°, and dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

Attempts to reduce esperitin were unsuccessful, possibly owing to the hindering action of the free phenolic hydroxyl groups, or perhaps owing to some influence of the solvent. R. V. S.

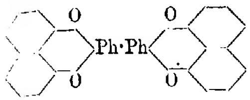
Phenylhydroxyketoperinaphthindene. MARCELLO CESARIS (*Gazzetta*, 1912, **42**, ii, 453—472).—When phenylacetic acid, naphthalic anhydride, and potassium acetate are heated at 230° for two hours, 1-hydroxy-3-keto-2-phenylperinaphthindene (annexed formula) is formed; it crystallises in iridescent, orange-yellow scales, m. p. 218°, and dissolves in concentrated sulphuric acid, giving an intense yellow coloration. The substance dissolves in alkalis, and is reprecipitated by acids. The *acetyl* derivative, $C_{19}H_{11}O_2Ac$, forms deep yellow needles, m. p. 172—175°. Bromination of hydroxyketophenylperinaphthindene in anhydrous solvents (such as chloroform) yields an unstable *additive product* of the probable formula $C_{19}H_{12}O_2Br_2$,HBr. By the action of water on this compound, or by bromination in aqueous solvents, 2-*bromo*-1 : 3-*diketo*-2-*phenylperinaphthindene* (annexed formula) is obtained; it forms prisms or needles, m. p. 198°. The *anilide*, $C_{19}H_{11}O_2$·NHPh, prepared from the bromo-derivative, crystallises in golden-yellow scales, m. p. 225—227°. When the bromo-derivative is treated with alkalis, hydroxyketophenylperinaphthindene





is obtained. The action of hydrogen bromide on hydroxyketophenylperinaphthindene (in chloroform) yields an unstable *compound*, $C_{19}H_{12}O_2HBr$, which begins to melt at 90° and is completely melted at 210°.

Cautious oxidation of hydroxyketophenylperinaphthindene with permanganate yields naphthalic acid, benzoic acid, and traces of an *acid* crystallising in colourless needles, m. p. about 200—202°. Oxidation with potassium dichromate in acetic acid yields a neutral substance, $C_{38}H_{22}O_4$, to which the annexed structure of *bis-diketophenylperinaphthindene* is ascribed; it is a straw-coloured, crystalline powder, m. p. about 235—236° (decomp.), and it dissolves in concentrated sulphuric acid, giving an intense orange-red coloration. R. V. S.



Preparation of α-Chloroanthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252578).—When α-nitroanthraquinone (or its derivatives) is treated with chlorine, this element displaces the α-nitro-group. Moreover, when 1-nitro-2-methylanthraquinone is similarly treated at high temperatures it furnishes ω-di- with some ω-mono- and ω-tri-chloro-derivatives. 1-Chloroanthraquinone is obtained (in satisfactory yield) when 1-nitroanthraquinone (80 parts) in 400 parts of trichlorobenzene is treated at 160—165° with a stream of chlorine; 1 : 5-dinitroanthraquinone at 190° furnishes 1 : 5-dichloroanthraquinone, and at 160—180° 1-nitro-2-methylanthraquinone yields chiefly ω-1-trichloro-2-methylanthraquinone. F. M. G. M.

Preparation of Condensation Products of the Anthracene Series Containing Sulphur. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251115).—When negatively substituted anthraquinones which in addition contain one or more auxochrome groups are condensed with arylmercaptols they yield compounds which can be employed as pigments, or for the preparation of dyes.

The *compound* obtained when an alcoholic solution of 4-chloro-1-hydroxy-2-methylanthraquinone (54 parts) containing 13 parts of potassium hydroxide is heated at 100° with *p*-tolyl mercaptan (25 parts) is a crystalline, violet powder. The following *compounds* obtained in a similar manner are described in the original; from *p*-tolyl mercaptan with (1) 4-chloro-1-amino-2-methylanthraquinone a glistening, bronze, crystalline powder; (2) with 4-bromo-1-methylaminoanthraquinone, glistening, violet needles; (3) with 1-chloroaminoanthraquinone an orange, crystalline powder; whilst 2-bromo-1-amino-4-hydroxyanthraquinone furnishes 1-*amino*-4-*hydroxyanthraquinone* 2-p-*tolyl thioether*, violet-brown bronze needles, and 2 : 3-dichloro-1 : 4-diaminoanthraquinone yields 1 : 4-*diaminoanthraquinone* 2 : 3-*dithio*-p-*tolyl ether*, blue needles. F. M. G. M.

Preparation of Anthracene Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252530. Compare A., 1907, i, 1067).—An account of the preparation of *compounds* of cœrthionium type by heating the following anthraquinone thio-ethers with concentrated sulphuric acid at 150—160°: αα′-dianthraquinonyl thioether; αβ-dianthraquinonyl thioether; 4 : 4′- or 5 : 5′-dibenzoyldi-

amino-1 : 1'-dianthraquinonyl thioether, whilst the condensation of 1 : 5-dichloroanthraquinone (1 mol.) with 2 mols. of anthraquinone-2-mercaptol (compare A., 1907, i, 1067) furnishes 1 : 5-*anthraquinonedimercaptol-di-2'-anthraquinonyl thioether.* F. M. G. M.

Binuclear Quinones of the Anthraquinone Group. HANS MEYER, RICHARD BONDY, and ALFRED ECKERT (*Monatsh.*, 1912, 33, 1447—1468).—The supposed oxidation of dihydrodianthrone by amyl nitrite (Padova, A., 1909, i, 167, 655) to dianthrone is apparently a mistake, as the product is a mixture of anthraquinone with unchanged dihydrodianthrone. *Dianthrone*,

$$CO{<}{\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}}{>}C{=}C{<}{\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}}{>}CO,$$

can, however, be easily obtained by the oxidation of dianthranol in alkaline solution with potassium persulphate or hydrogen peroxide; the product, a crystalline powder, is preceded by an intermediate labile green *substance*. If a solution of dianthrone in acetic acid is exposed to sunlight or to the rays from a mercury lamp or an electric arc, it deposits yellow needles of *meso*-naphthadianthrone, $CO{<}{\genfrac{}{}{0pt}{}{C_6H_3}{C_6H_3}}{>}C{=}C{<}{\genfrac{}{}{0pt}{}{C_6H_3}{C_6H_3}}{>}CO$ (compare Scholl, Mansfield, and Potschiwauscheg, A., 1910, i, 494); the different properties of the substance described earlier are shown to be due to impurity, as the purified substances give practically identical absorption spectra. The substance gives an orange vat, it dissolves in sulphuric acid to a red fluorescent solution, and is oxidised by chromic acid to anthraquinone. The hydrogen liberated during the above conversion of dianthrone into *meso*-naphthadianthrone is probably largely oxidised by oxygen dissolved in the solvent; also, if an atmosphere of carbon dioxide is used, it is observed that some carbon monoxide is formed; only 95% of the original substance is obtained as *meso*-naphthadianthrone, whilst the solvent is found to contain afterwards about 2% of a volatile *hydrocarbon*, leaflets, m. p. 62—63°, possibly hexahydroanthracene, and also a little anthraquinone.

When anthraquinone is submitted in acetic acid to the action of nascent hydrogen (tin and hydrochloric acid) in intense light, the usual products, anthranol and dianthryl, are accompanied by a considerable quantity of dihydroanthracene.

By stopping the action of light on dianthrone at an early stage, dianthranol is found to be present, and is presumably the primary product from which the other substances above are subsequently formed; this idea is supported by the plentiful formation of diacetyldianthranol when a hot solution of dianthrone in acetic anhydride is exposed to light. Diacetyldianthranol in boiling solution when exposed to light for a considerable time is converted largely into a crystalline *substance*, m. p. circa 300°, and a little *meso*-naphthadianthrone.

Helianthrone (Scholl and Mansfield, *loc. cit.*), dissolved in acetic acid and exposed to light, deposits rhombic leaflets of a substance which on crystallisation from nitrobenzene separates in the characteristic needles of *meso*-naphthadianthrone; the identity of

the product was proved by its absorption spectrum. The yield was over 90%, and was accompanied by a brown, amorphous substance possessing the properties of a hydro-derivative of helianthrone.

D. F. T.

Preparation of Borneol and *iso*Borneol Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252158).—*Borneyl cinnamate*, b. p. 215°/10 mm., when treated with bromine (in carbon tetrachloride solution) yields *borneyl dibromo-β-phenylpropionate*, colourless, glistening crystals, m. p. 73°; this ester can also be prepared by the action of dibromo-β-phenylcinnamoyl chloride on borneol in the presence of pyridine; the corresponding iso*borneyl* ester forms colourless, glistening leaflets, m. p. 69°.

When *borneyl phenylpropiolate*, b. p. 230—235°/19 mm., is treated with bromine it furnishes *borneyl bromocinnamate*, colourless crystals, m. p. 76°, which is also procurable from borneol and bromocinnamoyl chloride.

Borneyl o-*chlorocinnamate*, colourless crystals, m. p. 102—108° (probably a mixture of two isomerides), on bromination yields *borneyl* o-*chloro-αβ-dibromophenylpropionate*, colourless prisms, m. p. 91°.

αβ-Dibromo-m-*methoxy-β-phenylpropionyl chloride*, m. p. 189°, yields a *borneyl* ester, m. p. 63—64°; *borneyl dibromocinnamate* has m. p. 65°, and *borneyl αβ-dibromo-β*-p-*tolylpropionate*, m. p. 90—91°.

These esters are of therapeutic value. F. M. G. M.

Preparation of Odourless or Faintly Odorous Esters from Valeric Acid and Therapeutically Powerful Alcohols. J. D. RIEDEL (D.R.-P. 252157).—iso*Valerylglycylborneyl* ester, a viscous liquid, b. p. 181°/12 mm., D^{20} 1·027, is prepared by stirring together borneyl chloroacetate and sodium valerate until the separation of sodium chloride is complete; the corresponding iso*borneyl* ester has b. p. 182—183°/12 mm. and D^{15} 1·0318, whilst the iso*valerylglycylmenthyl* ester has b. p. 197°/19 mm. and D^{16} 0·986. F. M. G. M.

Δ^4-Menthen-3-one. OTTO WALLACH, RUD. MÜLLER, and FR. HENJES (*Chem. Zentr.*, 1912, [ii], 922—923; from *Nachr. K. Ges. Wiss. Gött.*, 1912, 431—436).—In order to confirm the description and constitution already assigned to Δ^4-menthen-3-one (A., 1908, i, 813), the authors have prepared it from (*a*) Δ^4-menthene, made from 1 : 4-*cyclo*hexanone, and (*b*) *d*-menthene, obtained from menthol, and find that the characters of these two preparations are the same as those already given. The active specimen had $[\alpha]_D^{18}$ $-67·46°$ in methyl alcohol. The low boiling point of the ketone is probably due to the position of the *iso*propyl side-chain between a :CO group and an ethylenic linking. The latter probably renders reactive the hydrogen atom in position 6, whilst the :CO group confers reactivity on the neighbouring H-atom (position 2), and this joint action explains the formation of a dibenzylidene derivative from this ketone. No thymol is produced on oxidation with ferric chloride in acetic acid. T. A. H.

Hydrogenation with Platinum Metals as Catalyst. VI. ALADAR SKITA (*Ber.*, 1912, 45, 3312—3318. Compare A., 1911, i, 1017).—Azobenzene in alcoholic solution is readily reduced by

hydrogen under a pressure of two atmospheres in the presence of colloidal palladium with gum arabic as the protecting colloid. The reduction to hydrazobenzene takes place rapidly, whereas the reduction of the hydrazobenzene to aniline proceeds comparatively slowly.

[With W. A. MEYER and JULIUS VON BERGEN.]—Under conditions similar to those used with azobenzene, α-ionone is reduced to *dihydro-α-ionone*, $C_{13}H_{22}O$, which is a liquid, b. p. 121—122°/14 mm., possessing a slight odour of cedar wood, but the characteristic odour of the α-ionone has disappeared. Similarly, β-ionone gives *dihydro-β-ionone*, b. p. 126—129°/12 mm., possessing properties resembling those of the α-compound. Both the dihydro-compounds on further reduction give the same *tetrahydroionone*, $C_{13}H_{24}O$, b. p. 126—127°/13 mm., showing that it is the ethylene linking in the side-chain which is first reduced.

Tiemann (A., 1898, i, 376) has expressed the opinion that ionone acts as a perfume because of the αβ-ethylene linking in the side-chain. If this is so, a dihydroionone which has been hydrogenised in the nucleus, and still contains an αβ-ethylene linking in the side-chain should still be a perfume. To prepare such a compound, dihydro*cyclo*-citral was acetylated in tartaric acid solution by a method similar to that used in preparing ψ-ionone from citral and acetone. The *dihydroionone*, $C_{13}H_{22}O$, thus obtained was a pale yellow liquid, b. p. 124—125°/14 mm., and having an odour similar to that of ionone. Since only the latter compound possesses the character of a perfume, the authors propose that the name dihydroionone should be retained for it, whilst the dihydro-compounds obtained from the α- and β-ionones should be termed 1 : 1 : 3-trimethyl-Δ^3- and 1 : 1 : 3-trimethyl-Δ^2-*cyclo*-hexenylethyl methyl ketones respectively.

ψ-Ionone when hydrogenised gives *tetrahydro-ψ-ionone*,

$$CMe_2{:}CH{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}COMe,$$

b. p. 126—127°/14 mm.

In the unsaturated aldehydes and ketones hitherto examined, with the exception of mesityl oxide (A., 1910, i, 71) and phorone (A., 1909, i, 479), the hydrogenation does not affect the carbonyl group. Acraldehyde also forms an exception, giving allyl alcohol together with propaldehyde.

[With FRIEDRICH NORD.]—The following alkaloids have been hydrogenised by method similar to that used with quinone and cinchonine (A., 1911, i, 1017), the protecting colloid not being used. Quinidine gives *dihydroquinidine*, $C_{20}H_{26}O_2N_2,H_2O$, m. p. 165°, $[\alpha]_D^{20}$ +265·3°; the *methiodide*, $C_{22}H_{27}O_2N_2I$, forms slender, light yellow needles, m. p. 224—225°, and the *phosphate*, $C_{20}H_{29}O_6N_2P$, decomposes at 212°. Cinchonidine gives *dihydrocinchonidine*, $C_{19}H_{24}ON_2$, m. p. 229°, $[\alpha]_D^{20}$ −97·5°, the *methiodide*, $C_{20}H_{27}ON_2I$, and *phosphate*, $C_{19}H_{27}O_3N_2P$, of which have the m. p.'s 248° and 113° respectively. The dihydroquinidine is identical with the naturally-occurring hydroconquinine, and the dihydrocinchonidine with hydrocinchonidine. T. S. P.

[Glycuronic Acids Produced by the Coupling of Alicyclic Compounds in the Organism.] JUHO HÄMÄLÄINEN (*Skand. Arch. Physiol.*, 1912, 27, 141—226).—See this vol., i, 133.

The Simultaneous Action of Catalysts. VLADIMIR N. IPATIEV (*Ber.*, 1912, **45**, 3205—3218. Compare A., 1911, i, 31).—[With N. MATOV.]—In order to prepare fenchane from fenchone, the latter was first heated with hydrogen under pressure (110 atmos.) for twenty hours at 240°, whereby fenchenol, b. p. 196°/752 mm. and D^{20} 0·9554, was obtained. Attempts to prepare fenchene, which could then be hydrogenised to fenchane, from fenchenol by the fission of water under the catalytic action of alumina at temperatures varying from 210° to 255° gave only very small yields, and the use of the bromo-compound gave no better results. When, however, fenchenol was heated at 215° for twelve to fourteen hours with hydrogen under a pressure of 110 atmos., in the presence of a mixture of nickel oxide and alumina as catalysts, fenchane was obtained directly; $[\alpha]_D$ − 19·83°, D^{17} 0·8766, D^{20} 0·8733, n^{17} 1·45409.

The hydrogenisation of commercial camphene (m. p. 48·5°, b. p. 160—165°/761 mm.) in the presence of nickel oxide at 240° gives *iso*camphane, m. p. 53·5—57°, b. p. 162·5—163·5°/758 mm., D^{19} 0·8457.

Attempts to prepare camphene by the dehydration of borneol in the presence of alumina at 350—360° gave only small yields of a liquid camphene, together with large quantities of oxidation products, the reaction being a very slow one. When, however, borneol (m. p. 208—210°, b. p. 215°, $[\alpha]_D$ + 30·21°) is hydrogenised at 215—220° under 110 atmos. pressure in the presence of a mixture of nickel oxide and alumina, *iso*camphane is obtained, m. p. 63—64·5°, b. p. 164°/757 mm., D^{70} 0·84157, $[\alpha]_D$ − 8·50°. Under similar conditions, *iso*borneol (m. p. 209°, b. p. 211°, $[\alpha]_D$ − 1·82°) also gives rise to *iso*camphane, m. p. 62·5—64°, b. p. 164—164·5°/756·1 mm., D^{70} 0·84293, $[\alpha]_D$ − 2·81°. When heated with alumina alone at 350—360°, *iso*borneol yields small quantities of crystalline camphene, together with considerable quantities of condensation products.

The transformation of cyclic ketones into the saturated hydrocarbons by the combined action of reduction and dehydration catalysts takes place readily, at much lower temperatures than in the reduction of the alcohols. In the presence of a mixture of nickel oxide and alumina at 200°, carvomenthone is readily reduced to menthane by hydrogen under pressure. Similarly, camphor (m. p. 174·5—176°, b. p. 203·5°/743·2 mm., $[\alpha]_D$ + 33·20°) at 200° gives *iso*camphane (m. p. 64·5—65·5, b. p. 164—165°/757 mm., D^{70} 0·8462, $[\alpha]_D$ − 3·95°). Comparison of the physical properties of the various *iso*camphanes prepared from camphene, borneol, *iso*borneol, and camphor shows that they are very similar to each other.

When a mixture of alumina and copper oxide is used instead of alumina and nickel oxide as catalyst, terpene alcohols give rise to unsaturated hydrocarbons. The temperature of dehydration is much lower, being 220° instead of 360°, and in consequence of this lower temperature there is no hydrogenisation of the double linking in the presence of the copper oxide. Under such conditions borneol at 200—220° and a hydrogen pressure of 50 atmos., gives a mixture of solid and liquid camphene, the former having m. p. 60—62·5°, b. p. 156—159°/763 mm., D^{70} 0·85075, and the latter b. p. 155—160°/

763 mm., D^{16} 0·8688, $[\alpha]_D$ 1·61°, n^{16} 1·45819. This liquid camphene yields a chloride, m. p. 140°, and when hydrogenised in the presence of nickel oxide gives liquid *iso*camphane, b. p. 160—165°, D^{18} 0·85204, n^{18} 1·45009.

Under the same conditions as with borneol, *iso*borneol gives rise only to a solid camphene, m. p. 53·5°, b. p. 162—167°/766 mm., D^{70} 0·85092, n^{60} 1·44244.

[With O. ROUTALA.]—At 240°, in the presence of a mixture of alumina and copper oxide and under a hydrogen pressure of 20 atmos., 1-methyl*cyclo*hexan-2-ol yields methyl-Δ^1-*cyclo*hexene (compare A., 1911, i, 25), b. p. 107·5—108·5°/759·5 mm., D_4^{18} 0·8063, n^{18} 1·44094. The *nitrosochloride*, C_7H_{12}·NOCl, m. p. 102°, is very unstable, decomposing in a desiccator with the formation of the *oxime*, C_7H_{10}:NOH. The *nitrosate*, $C_7H_{12}O_4N_2$, has m. p. 115°. By the addition of hydrogen bromide in acetic acid solution, 1-*bromomethyl*cyclo*hexane* is obtained as a colourless liquid, b. p. 156—160°, D^{18} 1·2544, n^{18} 1·48168. The action of silver oxide on this compound gives rise to small quantities only of the alcohol, the methyl*cyclo*hexene being regenerated for the most part. With silver acetate, however, the *acetic* ester, $C_9H_{16}O_2$, is readily obtained, b. p. 182—187°, D^{18} 0·9536, n^{18} 1·43862, which, on saponification with alcoholic alkali gives 1-*methyl*cyclo*hexan*-1-*ol*, $C_7H_{14}O$, b. p. 159—164°/759 mm., D^{18} 0·9417, n^{18} 1·45179.

Attempts to prepare the bromide from 1-methyl*cyclo*hexan-2-ol by the action of phosphorus tribromide were unsuccessful, owing to the ready fission of hydrogen bromide.

To explain the greater catalytic effect of the combined catalysts, it is assumed that a labile complex, for example, NiO,Al_2O_3, is formed as an intermediate product, and then decomposes, giving the components in the nascent state. The combined action of the catalysts is called "hydrolytic reduction." T. S. P.

Constituents of Ethereal Oils. The Sesquiterpene Selinene and its Derivatives. FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, 45, 3301—3307. Compare Schimmel, A., 1910, i, 328).—Selinene, $C_{15}H_{24}$, the sesquiterpene from celery seed oil, which has b. p. 128—132°/11 mm., D^{20} 0·9190, n_D 1·5092, $[\alpha]_D$ + 61°36′, is shown to be a bicyclic doubly unsaturated hydrocarbon. On reduction with hydrogen in presence of finely divided platinum, or of the dihydrochloride with sodium and alcohol, *tetrahydroselinene*, $C_{15}H_{28}$, is obtained, b. p. 126—128°/10·5 mm., D^{20} 0·8881, n_D 1·48259, $[\alpha]_D$ + 7°.

When selinene dihydrochloride is treated with calcium hydroxide, one halogen atom is eliminated as hydrogen chloride, and the other replaced by hydroxyl, the alcohol *selinenol*, $C_{15}H_{26}O$, being obtained; it has b. p. 155—163°/19 mm., D^{20} 0·9627, n_D 1·50895, $[\alpha]_D$ + 52°36′. On reduction, *dihydroselinenol*, crystallising in colourless needles, m. p. 86—87°, is obtained. The preparation of this compound is the best method of detecting selinene. E. F. A.

Extraction of Coffee Oil. VIKTOR GRAFE (*Monatsh.*, 1912, 33, 1389—1406. Compare Erdmann, A., 1902, i, 551).—From a comparison with ordinary coffee beans and beans which have been previously deprived of caffeine, it is found that the latter give less coffee oil, the

shortage being especially in the furfuryl alcohol of the mixture. Beans freed from skin and wax gave practically the same results as ordinary beans, so that the parent substance of the coffee oil must have been still present. It is believed that the treatment preceding the extraction of the caffeine diminishes the content of fibrous matter, and causes partial decomposition of the chlorogenic and coffalic acids; these acids are regarded as the source of the valeric acid in coffee oil, whilst the fibrous matter is the origin of the furfuryl alcohol.

D. F. T.

Desulphuration of Vulcanised Rubber. PAUL ALEXANDER (*Chem. Zeit.*, 1912, **36**, 1289—1291, 1340—1342, 1358—1359).—The author has stated previously (*ibid.*, 1910, **34**, 789) that it is impossible to remove the combined sulphur from vulcanised rubber without destroying the rubber substance. The work of Hinrichsen and Kindscher (A., 1912, i, 706) having placed this conclusion in doubt, the author has repeated and extended this work.

Para rubber was vulcanised by mixing it with varying quantities (5 to 20 parts) of sulphur and heating at 143° under 4 atmospheres pressure. The products (A—E) were then treated in benzene solution with (1) alcoholic sodium hydroxide; (2) alcoholic sodium hydroxide in presence of zinc, magnesium or calcium, and the materials (A_1A_2, B_1B_2, C_1C_2, etc.) thus obtained examined in comparison with the original products. The results are too numerous to quote, but the most interesting are the "vulcanisation-coefficients" arrived at in three different ways: (1) calculated from the total sulphur, less the sum of the sulphur in the ash and that in the "matter soluble in acetone"; (2) calculated from the sulphur in the "matter insoluble in acetone," less the sulphur in the ash, and (3) the sulphur in the nitrosite prepared from the product under examination. From the whole of his results the author draws the conclusion that the last method gives the true vulcanisation-coefficient, that is, the amount of sulphur which combines with 100 parts of pure rubber. The following general conclusions are drawn: The methods described, which are those of Hinrichsen and Kindscher, do not remove combined sulphur from vulcanised rubber, but actually increase the amount in combination when insufficient sodium hydroxide to combine with all the free sulphur is used. The metals used exert no action in this direction. The whole of the free sulphur is not removed from vulcanised rubber by extraction with acetone, probably because part of it at the temperature of vulcanisation is converted into a modified form, which is insoluble in acetone, but dissolves in alcoholic sodium hydroxide. The products (A_1A_2, etc.) referred to above contain "depolymerised rubber," which is soluble in acetone; this material is produced by the heat applied, and not by the action of the alkali hydroxide or the metals or solvents used. The rest of the paper is polemical in favour of Loewen (A., 1912, ii, 914, 915) against Hinrichsen and Kindscher (A., 1912, i, 1007).

T. A. H.

Resin of Pinus Halepensis. L. REUTTER (*J. Pharm. Chim.*, 1912, [vi], **6**, 497—500).—This resin has m. p. 83—85°, acid number

180·75—182·74, saponification number 196·5—199·3, ester number 15·7—16·5, and gives colour reactions similar to those of cholesterol. The portion soluble in ether yields to aqueous ammonium carbonate, *helepinic acid*, $C_{21}H_{40}O_4$, m. p. 73·5—74·5°, and subsequently to aqueous sodium carbonate: (1) *helepinolic acid*, $C_{40}H_{56}O_5$, m. p. 144·2—145·5°, which is crystalline and yields a *silver* salt; (2) *a-helepinolic acid* $C_{34}H_{50}O_4$, m. p. 80·5—81·5°, which is soluble in alcohol, but yields a lead salt insoluble in that solvent; (3) *β-helepinolic acid*, $C_{18}H_{28}O_4$, m. p. 80·5—82°, which is soluble in alcohol and yields a *lead* salt also soluble in alcohol, and (4) *heleponic acid*, $C_{18}H_{28}O_2$, m. p. 156—157°, separating from methyl alcohol in crystals. The resin also contains 14·4% of volatile oil (compare Tschirch and Schulz, A., 1907, i, 544).

T. A. H.

The Resinous Exudation of Pinus Pinea. L. REUTTER (*J. Pharm. Chim.*, 1912, [vi], 6, 494—497).—The portion of the oleo-resin soluble in ether yielded on extraction with (1) aqueous ammonium carbonate, *pineic acid*, $C_7H_{14}O_4$, m. p. 99—99·5°, and (2) aqueous sodium carbonate, *pineolic acid*, $C_{18}H_{28}O_3$, m. p. 86°, and a very small amount of a substance giving a precipitate with alcoholic lead acetate. The portion insoluble in ether on steam distillation yielded *pineareseen*, $C_9H_{13}O_4$, m. p. 85°, and a volatile oil, which had an odour recalling that of turpentine, and when kept deposited colourless crystals, m. p. 204°, with an odour similar to that of borneol.

T. A. H.

Chemical Composition of Dulcamara. GEORGES MASSON (*Chem. Zentr.*, 1912, ii, 366—367; from *Bull. Sci. Pharm.*, 1912, 19, 283—289. Compare Desfosses, *Jahresb.*, 1820, 2, 114; Davis, A., 1902, ii, 686).—The aërial portion of dulcamara is free from solanine, but contains in addition to proteins, gums, and reducing sugars, dulcamaretic acid, dulcamaric acid, and solacein (1%). The two acids are both soluble in alcohol, but the first only is soluble in ether, and they can be separated by the use of this solvent.

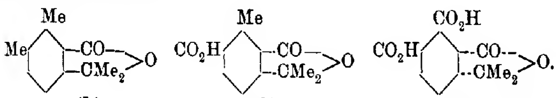
Dulcamaric acid is a glucosidic saponoid; it forms a greenish-brown powder, m. p. 190° (decomp.), and yields brown, amorphous salts with alkalis. On hydrolysis with 7% sulphuric acid in alcohol it furnishes (1) *dulcamarigenic acid*, m. p. 160°, and (2) a reducing sugar, which gives a *phenylosazone*, m. p. 196—197°, crystallising from boiling water in slender needles.

Dulcamaretic acid, m. p. 90—92°, is a non-glucosidic saponoid; it forms a green buttery mass, giving green, amorphous alkali salts. It could not be hydrolysed.

Solacein, m. p. 236—237°, is a nitrogenous glucoside; it forms a colourless, amorphous mass, soluble in alcohol, but insoluble in ether or water, and reduces auric chloride or silver nitrate on warming, but not Fehling's solution. It yields a yellow *platinichloride*, a stable *sulphate*, and a gelatinous *hydrochloride*. On hydrolysis by acids it furnishes solanidine, m. p. 190°, and a sugar from which a *phenylosazone*, m. p. 171—172°, crystallising in needles from methyl alcohol, was prepared.

Dulcamarin is regarded as an alkali compound of the two acid saponoids. T. A. H.

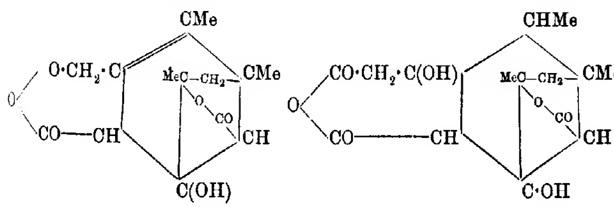
Picrotoxin. Francesco Angelico (*Gazzetta*, 1912, 42, ii, 540—545. Compare A., 1911, i, 1003).—When the ketone, $C_{14}H_{16}O_3$ (obtained by the action of hydriodic acid and red phosphorus on picrotoxin, as already described), is heated with concentrated alcoholic potassium hydroxide, a new *compound*, $C_{12}H_{14}O_2$ is obtained in good yield. This substance crystallises in large, colourless needles, m. p. 81°, b. p. 290°; it is volatile with steam and has an odour of celery like the phthalides. It is stable towards oxidisers and reducers, but when heated at 260—280° with three times its weight of powdered potassium hydroxide, it yields acetone and 2:3-dimethylbenzoic acid, the barium salt of which gives *o*-xylene when distilled with barium oxide. When the phthalide, $C_{12}H_{14}O_2$, is oxidised with nitric acid, it yields an *acid*, $C_{12}H_{14}O_4$, of the probable constitution II, whilst when it is oxidised with alkaline potassium permanganate it yields an *acid*, $C_{12}H_{10}O_6,H_2O$, of the probable formula III. This acid gives a fluorescein with resorcinol, and when fused with potassium hydroxide yields acetone and 1:2:3-benzenetricarboxylic acid. The acid, $C_{12}H_{10}O_6,H_2O$, loses H_2O at about 130°, and gives potassium and silver salts. In view of these reactions, the compound, $C_{12}H_{14}O_2$, probably has the structure indicated in formula I.



(I.) (II.) (III.)

The phthalide has been obtained by other means (but not identified) by Sielisch (A., 1912, i, 886).

The ketone, $C_{14}H_{16}O_3$, from which the phthalide is obtained, also loses acetone when fused with potassium hydroxide, and probably contains the keto-methylenic grouping, since the action on it of amyl nitrite and sodium ethoxide gives an oximino-compound, m. p. 215° (decomp.), which is converted by hydroxylamine into a dioxime. In consequence of these results and of those formerly published, the author regards picrotoxinine and picrotin, not as hydronaphthalene derivatives, but as hydrobenzene derivatives, related to *cyclo*hexene and *cyclo*hexane respectively. He suggests, therefore, the following provisional formulæ for the two substances:



R. V. S.

Picrotinic Acids. PAUL HORRMANN (*Ber.*, 1912, **45**, 3434—3437).—Angelico has given the formula $C_{15}H_{18}O_8$ to α-picrotinic acid and $C_{17}H_{24}O_8$ to its ethyl ester (A., 1910, i, 404). One or other of these formulæ must be wrong. The author shows that α-picrotinic acid has the formula $C_{15}H_{20}O_8$, decomp. 258°, and is identical with Horrmann and Seydel's δ-picrotinic acid (A., 1912, i, 1008). It is not an oxidation product of picrotin, but is produced merely by the addition of water. C. S.

Tannin. KARL FEIST (*Arch. Pharm.*, 1912, **250**, 668—683).—The author has stated previously that "Turkish" galls contain glucogallic acid and a tannin, which yields dextrose on hydrolysis by acids (A., 1912, i, 566, 888). These two substances are now described.

"Turkish" galls were extracted in turn with chloroform, benzene, and dry ether. The chloroform extract contained chlorophyll, *cyclo*-gallipharic acid, and gallic acid. Benzene removed nothing of importance. The ether extract consisted of glucogallic acid and a little tannin. The former was isolated by dissolving the dry extract in acetone, allowing the latter to evaporate, and pouring off the mother liquor as long as amorphous matter separated. Eventually *glucogallic acid* separated in rosettes of greyish needles. It can be prepared in like manner from commercial tannin derived from "Turkish" galls. Glucogallic acid, m. p. 233° (decomp. anhydrous), $[\alpha]_D^{17} + 10{\cdot}6°$ in acetone, contains when air-dry about 12% of water, and has a molecular weight, when dry, of about 318 as determined by titration (assuming 1 CO_2H group) or by the b. p. method. On hydrolysis by boiling with *N*-sulphuric acid it yields dextrose and gallic acid. It reduces Fehling's solution on boiling, and yields a semi-crystalline *methyl* derivative, m. p. 79°, which, unlike the acid itself, gives no coloration with ferric chloride, and does not reduce Fehling's solution. Glucogallic acid is not decomposed by emulsin, so that it is probably an α-glucoside; it probably does not contain a free ·CHO group.

The partly exhausted galls were next extracted with hot acetone. The *tannin* (designated "Turkish" tannin to distinguish it from that obtained from "Chinese" galls) had $[\alpha]_D + 28{\cdot}6°$ to $+31°$, and molecular weight 615—746 (b. p. method). On treatment with diazomethane in ether, part of it dissolved and was methylated (compare Herzig and Tscherne, A., 1905, i, 354). On hydrolysis the tannin yields dextrose and gallic acid; no glucogallic acid could be obtained as an intermediate product in this hydrolysis (compare Fischer and Freudenberg, A., 1912, i, 471, 887).

The tannin of "Chinese" galls (A., 1912, i, 888) has a molecular weight 899—1045, and is partly methylated on treatment with diazomethane in ether. T. A. H.

Action of Nitric Acid and Silver Nitrate on Tannin. ROGER DOURIS and A. WIRTH (*Chem. Zentr.*, 1912, ii, 1360; from *Bull. Sci. Pharmacol.*, 1912, **19**, 403—407).—When a solution of tannin is boiled with nitric acid and silver nitrate, silver cyanide is precipitated, the maximum yield occurring with the proportions 2 grams of silver nitrate, 10 c.c. of nitric acid (40° Bé.), and 2 grams of tannin, made up

to 100 c.c. with water. With a mixture of twice this concentration, a very violent reaction results in the formation of oxalic acid. Gallic acid has the same effect, but with pyrogallol or quinol the product is masked by the large amount of reduced silver which is also formed.

J. C. W.

Ratanhine. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1912, **33**, 1379—1388).—Ratanhine occurs only exceptionally in ratanhin extract (compare Kreitmair, A., 1874, 1038).

A specimen which came into the author's possession had the composition $C_{10}H_{13}O_3N$, m. p. 252° (decomp.); *hydrochloride*, monoclinic crystals [$a:b:c=1\cdot0283:1:0\cdot5111$, $\beta=103\cdot77°$]; *copper* salt, deep violet prisms; *methyl* ester, m. p. 116—117°, monoclinic prisms [$a:b:c=0\cdot8096:1:0\cdot8107$, $\beta=116\cdot32°$]. On fusion with potassium hydroxide, ratanhine yielded *p*-hydroxybenzoic acid, whilst decomposition by heat gave a *base*; *hydrochloride*, $C_{10}H_{13}ON,HCl$, colourless prisms.

D. F. T.

Degradation of Bilirubin and Bilirubic Acid. HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1912, **45**, 3274—3280).—Previously only traces of bases have been obtained on reduction of bilirubin. On boiling for fourteen to sixteen hours with acetic acid and hydrogen iodide, cryptopyrrole, $NH<\begin{matrix}CH{=}CMe\\ CMe{:}CEt\end{matrix}$, is readily obtained. It is left undecided whether hæmopyrrole and phyllopyrrole are also present. The second degradation product, the isomeric phonopyrrolecarboxylic acid, was isolated in relatively considerable quantity. It is readily esterified by means of methyl alcohol and dry hydrogen chloride, a method which is also applicable to phonopyrrolecarboxylic acid. This ester forms a dark brownish-red picrate, whereas the picrate of the isomeric ester is a normal yellow colour.

Bilirubic acid when reduced in a similar manner yields cryptopyrrole in small quantity together with a large proportion of the isomeric phonopyrrolecarboxylic acid; a considerable amount of the bilirubic acid remains unattacked. The results are interpreted as in favour of the formula:

$$\begin{matrix}CEt\cdot CMe\\ CMe\cdot NH\end{matrix}>C\cdot O\cdot C<\begin{matrix}CMe\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H,\\ NH-CMe\end{matrix}$$

for bilirubic acid.

Methyl phonopyrrolecarboxylate crystallises in colourless, flat needles, m. p. 57—58°. The *picrate* forms reddish-brown needles with a marked lustre, m. p. 121—122°. The *picrate* of the isomeric *methyl phonopyrrolecarboxylate* crystallises in slender, yellow, concentrically-grouped needles, m. p. 107—108°. The free *ester* obtained from the picrate forms crystals, m. p. 47—48°.

E. F. A.

Bile Pigments. IV. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1912, **82**, 391—405).—In part already abstracted (preceding abstract). On oxidation of bilirubin after reduction with sodium amalgam, methyl ethylmaleinimide and the oxime of phonopyrrole

carboxylic acid are obtained. This observation makes the existence of a third pyrrole complex in bilirubin probable.

Methylethylmaleinimide is also obtained on oxidation of bilirubic acid together probably with the oxime of phonopyrrolecarboxylic acid.

E. F. A.

Transformation of an Alcohol into a Sulphide or a Peroxide by Hydrogen Sulphide or Hydrogen Peroxide. ROBERT FOSSE (*Compt. rend.*, 1912, **155**, 1019—1020).—Xanthhydrol reacts with hydrogen sulphide or hydrogen peroxide as does a basic hydroxide, giving rise respectively to a sulphide and a peroxide.

On passing a stream of hydrogen sulphide into a solution of xanthhydrol in acetic acid a white, microcrystalline deposit of *xanthyl sulphide*, $\left(O<{C_6H_4 \atop C_6H_4}>CH\right)_2S$, is obtained, which is decomposed by hydrochloric acid, giving hydrogen sulphide and unstable xanthyl chloride. *Xanthyl peroxide*, $\left(O<{C_6H_4 \atop C_6H_4}>CH\right)_2O_2$, is similarly prepared by the addition of hydrogen peroxide to the acetic acid solution of xanthhydrol. On boiling it with fuming hydrochloric acid, chlorine is evolved and a pyrryl salt is produced. The peroxide gives an orange-yellow solution in a mixture of acetic and hydrochloric acids, which with chlorides or bromides of gold or uranium yields double xanthyl metallic chlorides or bromides.

W. G.

Triphenylmethyl. XXI. Quinocarbonium Salts of the Hydroxyxanthenols. MOSES GOMBERG and C. J. WEST (*J. Amer. Chem. Soc.*, 1912, **34**, 1529—1569).—In an earlier paper (A., 1911, i, 737) it was stated that hydroxy- and methoxy-xanthenols yield colourless carbinyl chlorides which are capable of uniting with a metal haloid, a halogen, or hydrogen haloid to form coloured quinocarbonium salts (compare Gomberg and Cone, A., 1910, i, 55, 869). A study has now been made of the salts of *p*-, 1-, 2-, 3-, and -4-hydroxy- and -methoxy-phenylxanthenol and of 3 : 6-dihydroxyphenylxanthenol.

It has been found that the hydroxy- and methoxy-groups cause a deepening of the colour of the quinonoid derivatives from the yellow of phenylxanthenol to deep red except in the case of the 3-derivatives which are yellow. The presence of these groups increases the stability of the quinonoid compounds, but diminishes that of the benzenoid salts; it also increases the reactivity of the xanthones. The influence of acetoxy- and benzoxy-groups diminishes the tendency of the compounds to tautomerise into the quinonoid form. The constitution of the compounds is discussed.

I. p-*Hydroxyphenylxanthenol Compounds*.—p-*Anisylxanthenol*,

$$OMe\cdot C_6H_4\cdot C(OH)<{C_6H_4 \atop C_6H_4}>O,$$

m. p. 120—121°, prepared by adding xanthone to the product of the action of magnesium on *p*-anisyl iodide, separates from benzene in white, prismatic crystals, containing $\frac{1}{2}C_6H_6$, and from ether or acetone in large, monoclinic prisms. p-*Anisylquinoxanthenol chloride*

hydrochloride, $\begin{matrix} HCl,CHCl\cdot CH:C\text{———————}O \\ CH{=}CH\text{-}C:C(C_6H_4\cdot OMe) \end{matrix}\!\!>\!C_6H_4$, m. p. 110—115° (decomp.), prepared by saturating a benzene solution of the xanthenol, to which a little acetyl chloride has been added, with hydrogen chloride, forms dark red crystals. If this salt is suspended in benzene or light petroleum and a current of air passed through the mixture, the hydrogen chloride is removed, and p-*anisylxanthenol chloride*, $OMe\cdot C_6H_4\cdot CCl{<}^{C_6H_4}_{C_6H_4}{>}O$, m. p. 95—96°, is produced, which forms colourless crystals. When a solution of the chloride in benzene is shaken with molecular silver, an unsaturated compound, analogous to triphenylmethyl, is formed, which on exposure to the air is converted into the *peroxide*, $\left[O{<}^{C_6H_4}_{C_6H_4}{>}C(C_6H_4\cdot OMe)\right]_2O_2$, m. p. 214° (decomp.), obtained as a white, crystalline powder. The following additive compounds of the chloride are described: *ferrichloride*, m. p. 198—199°; *zincichloride*, m. p. 240—241°; *mercurichloride*, m. p. 185—186°; *perbromide*, m. p. 159—163° (decomp.); and *periodide*. p-Anisylxanthenol *ethyl ether*,

$$O{<}^{C_6H_4}_{C_6H_4}{>}C(OEt)\cdot C_6H_4\cdot OMe,$$

m. p. 156—157°, and *methyl ether*, m. p. 129—130°, form colourless crystals.

p-*Anisylquinoxanthenol bromide hydrobromide* is a dark brown, crystalline substance. The *bromide*, $OMe\cdot C_6H_4\cdot CBr{<}^{C_6H_4}_{C_6H_4}{>}O$, forms colourless crystals; its *zincibromide* has m. p. 224—225°; *mercuribromide*, m. p. 192—194°; *perbromide*, m. p. 174—175°, and *periodide*, m. p. 187—189°. *p*-Methoxyphenylxanthenol *perchlorate*, m. p. 192—193°; hydrogen sulphate, m. p. 117—118°, and *phosphate*, m. p. 124—125°, are described.

p-*Hydroxyphenylxanthenol*, $O{<}^{C_6H_4}_{C_6H_4}{>}C(OH)\cdot C_6H_4\cdot OH$, m. p. 149—150° (decomp.), prepared from *p*-anisylxanthenol by Baeyer's method (A., 1910, i, 251), crystallises in rosettes of colourless needles. The *perchlorate* has m. p. 255—256°, and the *hydrogen sulphate*, m. p. 240—245°. p-*Hydroxyphenylquinoxanthenol chloride hydrochloride*, $O{<}^{C_6H_4}_{C_6H_4}{>}C:C_6H_4{<}^{OH}_{Cl,HCl}$ or

$$O{<}^{C_6H_4\text{———}}_{C_6H_4(Cl,HCl)}{>}C\cdot C_6H_4\cdot OH,$$

m. p. 235—240°, forms dark red, iridescent plates. p-*Hydroxyphenylquinoxanthenol chloride*, m. p. 235—245° (decomp.), is obtained as a red powder by heating the hydrochloride in a vacuum at 130°; its *ferrichloride* has m. p. 156—157°; *zincichloride*, m. p. 222—223°; *mercurichloride*, m. p. 215—216°, and *perbromide*, m. p. 230—235°; the *periodide* is purple. p-*Hydroxyphenylquinoxanthenol bromide*, m. p. 258—260° (decomp.), is a red, crystalline powder. When *p*-hydroxyphenylxanthenol is heated at 110—120° for two hours, it loses a molecule of water and is converted into *xanthylene-*

quinomethane, $O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C<\begin{smallmatrix}CH:CH\\CH:CH\end{smallmatrix}>CO$, m. p. 287—288°, which has a green colour, and is readily hydrolysed by dilute acid or alcoholic potassium hydroxide with regeneration of *p*-hydroxyphenylxanthenol. If the quinone is treated with hydrogen chloride, *p*-hydroxyphenylquinoxanthenol chloride hydrochloride is produced, whilst by the action of hydrogen bromide, *p*-hydroxyphenylquinoxanthenol bromide is obtained. Acetic anhydride converts the quinone into *p*-acetoxyphenylxanthenol. The quinone unites with 1 mol. of methyl sulphate to form a red additive compound which yields *p*-anisylxanthenol on hydrolysis. By the action of phosphorus pentachloride the quinone is converted into *p*-chlorophenylxanthenol chloride (Gomberg and Cone, A., 1910, i, 57).

p-*Acetoxyphenylxanthenol*, $O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C(OH)\cdot C_6H_4\cdot OAc$, m. p. 145—146°, obtained by the action of acetic anhydride and sodium acetate on *p*-hydroxyphenylxanthenol, crystallises in long, slender, colourless needles. p-*Acetoxyphenylquinoxanthenol chloride hydrochloride*, $O<\begin{smallmatrix}C_6H_4\\C_6H_4(Cl,HCl)\end{smallmatrix}>C\cdot C_6H_4\cdot OAc$, m. p. 118—122° (decomp.), forms light red crystals. p-*Acetoxyphenylxanthenol chloride*,

$$O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CCl\cdot C_6H_4\cdot OAc,$$

is obtained in colourless crystals; its *ferrichloride* has m. p. 182°; *zincichloride*, m. p. 194°; *stannichloride*, m. p. 188°, and *mercurichloride*, m. p. 215°; the *perbromide* has an orange colour. The *peroxide*, $\left[O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C(C_6H_4\cdot OAc)\right]_2O_2$, has m. p. 211—212° (decomp.).

p-*Benzoxyphenylxanthenol*, $O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C(OH)\cdot C_6H_4\cdot OBz$, m. p. 181—182°, forms colourless crystals. p-*Benzoxyphenylquinoxanthenol chloride hydrochloride*, m. p. 143—145° (decomp.), varies in colour from yellow to orange-red. p-*Benzoxyphenylxanthenol chloride*, m. p. 175—176°, yields additive *compounds* with ferric chloride, m. p. 204—205°, and with zinc chloride; the *perchlorate* has m. p. 235—236°. p-*Benzoxyphenylxanthenol peroxide* has m. p. 218—219° (decomp.).

II. 1-*Hydroxy*-9-*phenylxanthenol Compounds*.—Hydroxy- and methoxy-xanthones combine much more readily with metal haloids than xanthone itself. The hydrogen haloid additive compounds are very unstable, and can only be prepared in absence of water. 1-Methoxyxanthone (Tambor, A., 1910, i, 559) yields the following compounds: *stannichloride*, m. p. 135—136°; *stannibromide*, m. p. 172—173°; *mercurichloride*, m. p. 183—184°; *mercuribromide*, m. p. 167—168°; *zincichloride* and *zincibromide*, and the *hydrochloride*, m. p. 110—115°.

1-*Methoxy*-9-*phenylxanthenol*, $OH\cdot CPh<\begin{smallmatrix}C_6H_4\\C_6H_3(OMe)\end{smallmatrix}>O$, m. p. 162—163°, prepared by adding 1-methoxyxanthone to a solution of magnesium phenyl bromide, forms lustrous, colourless needles; its *perchlorate* has m. p. 225°. 1-*Methoxy*-9-*phenylquinoxanthenol chloride*

hydrochloride, $O<{C_6H_4 \atop C_6H_3 \cdot OMe(Cl,HCl)}>CPh$, crystallises in lustrous, purple needles. 1-*Methoxy-9-phenylxanthenol chloride*,

$$O<{C_6H_4 \atop C_6H_3(OMe)}>CPhCl,$$

m. p. 160—161°, forms colourless crystals and yields coloured additive compounds with metal haloids. The *peroxide* has m. p. 200—201°.

1-*Hydroxy-9-phenylxanthenol*, $OH \cdot CPh<{C_6H_4 \atop C_6H_3(OH)}>O$, m. p. 148—150° (decomp.), forms colourless crystals, and yields a dark purple *perchlorate*, m. p. 249—250°. 1-Hydroxy-9-phenylxanthenol chloride could not be isolated, but its *ferrichloride*, m. p. 146—147°, and *stannichloride*, m. p. 185°, were prepared.

III. 2-*Hydroxy-9-phenylxanthenol Compounds*.—2-Methoxyxanthone furnishes the following additive compounds: *stannichloride*, m. p. 235—240°; *stannibromide*, m. p. 199—200°; *zincichloride*, m. p. 244—245°; *mercurichloride*, m. p. 200°; *mercuribromide*, m. p. 187—189°; *perchlorate*, m. p. 150—155°. 2-*Methoxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. 140—144° (decomp.), forms bright red crystals. 2-*Methoxy-9-phenylxanthenol chloride* has m. p. 198°, and yields a *ferrichloride*, m. p. 123—124°; *zincichloride*, m. p. 197—198°; *mercurichloride*; *stannichloride*, m. p. 147—149°, and *perbromide*. 2-*Methoxy-9-phenylquinoxanthenol bromide hydrobromide* forms deep red crystals and decomposes at 223—224°. 2-*Methoxy-9-phenylxanthenol bromide* is colourless, and yields coloured additive compounds with metal haloids; the *perchlorate* and *hydrogen sulphate* have m. p. 193—194° and 110—120° respectively.

2-Hydroxy-9-phenylxanthenol has m. p. 170°. 2-*Hydroxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. about 240°, is obtained as a dark red powder. 2-*Hydroxy-9-phenylxanthenol chloride* is colourless, and gives coloured additive compounds with metal haloids. 2-Hydroxy-9-phenylquinoxanthenol bromide (Kropp and Decker, A., 1909, i, 249) yields a *perchlorate*, m. p. about 260°, and *hydrogen sulphate*, m. p. 133—135°.

2-*Acetoxy-9-phenylxanthenol*, m. p. 151—152°, is a colourless, crystalline substance; the *perchlorate* has m. p. 180—185°. 2-*Acetoxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. 125—129° (decomp.), forms light orange crystals. 2-*Acetoxy-9-phenylxanthenol chloride* is colourless and gives coloured additive compounds with metal haloids. The *peroxide*, m. p. 128° (decomp.), forms white crystals.

2-*Benzoxy-9-phenylxanthenol*, m. p. 205—206°, is colourless; its *perchlorate* has m. p. 210°. 2-*Benzoxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. 147—148°, forms light red crystals. 2-*Benzoxy-9-phenylxanthenol chloride*, m. p. 190°, yields coloured additive compounds. The *peroxide* has m. p. 170° (decomp.).

IV. 3-*Hydroxy-9-phenylxanthenol Compounds*.—3-Hydroxyxanthone combines readily with metal and hydrogen haloids to form additive compounds. Phenyl-3-methoxyxanthenol (Decker and Fellenberg, A., 1907, i, 1065) has m. p. 125°, and its *perchlorate*, m. p. 215—217°. 3-*Methoxy-9-phenylxanthenol chloride* yields a *ferrichloride*, m. p.

163—164°; *zincichloride*, m. p. 200—201°, and *mercurichloride*, m. p. 190°. 3-*Methoxy*-9-*phenylquinoxanthenol bromide hydrobromide*, m. p. 112—115°, is orange-yellow and crystalline. The *zincibromide* of phenyl-3-methoxyxanthenol bromide has m. p. 150—155°.

3-*Hydroxy*-9-*phenylxanthenol* cannot be isolated, as it spontaneously loses water with formation of phenylfluorone. 3-*Hydroxy*-9-*phenylquinoxanthenol chloride hydrochloride*, prepared by the action of hydrogen chloride on phenylfluorone, forms yellow crystals. On passing dry air through a solution of this substance in benzene, 3-*hydroxy*-9-*phenylquinoxanthenol chloride*, $O<\begin{matrix}C_6H_4\\C_6H_3Cl(OH)\end{matrix}>CPh$, m. p. 198—200°, is produced as a yellow solid, which, when treated with molecular silver, is converted into phenylfluorone. 3-*Hydroxy*-9-*phenylquinoxanthenol bromide*, m. p. 238—240°, forms orange needles, and yields a *perchlorate*, m. p. 250°, and hydrogen sulphate, m. p. 201—202°.

V. 4-*Hydroxy*-9-*phenylxanthenol Compounds*.—4-Methoxyxanthone has m. p. 173—174°, and yields a *stannibromide*, m. p. 125—135°; *stannichloride*, m. p. 187—188°; *mercurichloride*, m. p. 204—205°; *perchlorate*, m. p. 160°; and *hydrobromide*. 4-*Methoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 144—145°, prepared from phenyl-4-methoxyxanthenol (Baeyer, A., 1910, i, 251), forms dark red, iridescent needles. 4-*Methoxy*-9-*phenylxanthenol chloride*, m. p. 237—238°, is colourless, and yields coloured additive compounds; the *ferrichloride* has m. p. 147—148°; *mercurichloride*, m. p. 205—207°; and the *zincichloride*, m. p. 240—241°. The *peroxide*, m. p. 202° (decomp.), forms colourless crystals. 4-*Methoxy*-9-*phenylquinoxanthenol bromide hydrobromide*, m. p. about 260°, separates in dark red crystals. The colourless bromide was not isolated, but the following coloured compounds were prepared: *zincibromide*, m. p. 234—235°; *mercuribromide*, m. p. 223°; *perbromide*, m. p. 188—189°.

4-Hydroxy-9-phenylxanthenol (Baeyer, *loc. cit.*) yields a *perchlorate*, m. p. 248—249°. 4-*Hydroxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 210—211°, forms dark red crystals. 4-*Hydroxy*-9-*phenylquinoxanthenol chloride* has m. p. 200—201°, and the corresponding *bromide*, m. p. 261—262°.

4-*Acetoxy*-9-*phenylxanthenol*, m. p. 127—128°, crystallises in colourless needles; its *perchlorate* has m. p. 190°. 4-*Acetoxy*-9-*phenylquinoxanthenol chloride hydrochloride* is an orange-red substance, which, when left in a desiccator, loses hydrogen chloride with formation of the colourless 4-*acetoxy*-9-*phenylxanthenol chloride*, m. p. 134—135°; this compound gives a *ferrichloride*, m. p. 136—137°, and a *zincichloride*, m. p. 160—165°. 4-*Acetoxy*-9-*phenylxanthenol peroxide*, m. p. 145—146°, forms colourless crystals.

4-*Benzoxy*-9-*phenylxanthenol* has m. p. 113—115°, and yields a *perchlorate*, m. p. 157—158°. 4-*Benzoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 85—90° (decomp.), crystallises in yellow needles. 4-*Benzoxy*-9-*phenylxanthenol chloride*, m. p. 111—112°, is colourless, and gives coloured additive compounds with metal haloids.

VI. 3 : 6-*Dihydroxy*-9-*phenylxanthenol Compounds*.—3 : 6-*Dihydroxy*-

9-*phenylquinoxanthenol chloride*, $O<\substack{C_6H_4(OH)-\\C_6H_3Cl(OH)}>CPh$, prepared by the action of hydrogen chloride on a solution of phenyl-3-hydroxyfluorone (Kehrmann and Dengler, A., 1908, i, 1002) in nitrobenzene or alcohol, forms yellow crystals containing 1 mol. of the solvent. The pure salt darkens at 250°, but does not melt at 275°. E. G.

The Benzeins of the Xyloquinols. FRIEDRICH KEHRMANN and TH. E. STILLER (*Ber.*, 1912, **45**, 3346—3349).—By modifying the process of preparation used for quinolbenzein chloride (Kehrmann, A., 1910, i, 408) it has been found possible to condense *o*- and *p*-xyloquinols with benzaldehyde.

o-Xyloquinolbenzein chloride (2 : 7-*dihydroxy*-9-*phenyl*-3 : 4 : 5 : 6-*tetramethylxanthonium chloride*), $CPh<\substack{C_6PhMe_2(OH)\\C_6HMe_2(OH)}>O{\cdot}Cl$, can be obtained by the careful action of benzaldehyde on a mixture of *o*-xyloquinol with the corresponding quinone in the presence of a mixture of equal parts of acetic acid and sulphuric acid; the *sulphate*, which separates in reddish-brown needles, when dissolved in water and treated with concentrated hydrochloric acid precipitates the chloride in brown needles or granules. The solution of the chloride when treated with sodium acetate solution deposits the free *base* in deep brownish-violet needles, for which the analysis indicates an equimolecular combination of anhydride and carbinol base (compare Kehrmann, *loc. cit.*); *platinichloride*, reddish-brown, crystalline powder. If an alkaline solution of the free base is carefully acidified with acetic acid and shaken with ether, the latter extracts the colourless carbinol base, which with more acetic acid turns yellow on account of the formation of the oxonium salt.

p-Xyloquinol was obtained by the reduction of *p*-xyloquinone prepared by the oxidation of *p*-xylidine (compare Noelting, Witt, and Forel, A., 1886, 57). The quinol was made to condense with benzaldehyde by a process similar to that which proved successful with the ortho-isomeride; the resultant p-*xyloquinolbenzein chloride* (2 : 7-*dihydroxy*-9-*phenyl*-1 : 4 : 5 : 8-*tetramethylxanthonium chloride*), deep red or blackish-brown crystals, on treatment in solution with sodium acetate precipitates the free *base* in bright yellow crystals; *platinichloride*, yellow crystalline powder. Unlike the analogous bases previously obtained, which dissolve in sodium hydroxide with a fleeting violet-colour, this base gives a yellow solution in sodium hydroxide.

D. F. T.

Ethers and Esters of Phthaleins and Benzeins of Orcinol. FREDRICH KEHRMANN [with E. ACKER, M. GUNTHER, and J. KNOP] (*Ber.*, 1912, **45**, 3505—3514).—By heating with methyl iodide, a solution of α-orcinolphthalein in dilute sodium hydroxide yields *α-orcinolphthalein dimethyl ether*,

$$O<\substack{C_6H_2Me(OMe)\\C_6H_2Me(OMe)}>C<\substack{C_6H_4\\O—}>CO,$$

m. p. above 365°, a white, crystalline powder, which exhibits a smaller

tendency than α-orcinolphthalein itself to form oxonium salts. By heating with methyl alcohol and concentrated hydrochloric acid, or by keeping for a month with methyl alcohol saturated with hydrogen chloride, it is converted into the dimethylated *methyl ester oxonium chloride*, $OCl{<}\begin{matrix}C_6H_2Me(OMe)\\C_6H_2Me(OMe)\end{matrix}{>}C{\cdot}C_6H_4{\cdot}CO_2Me$, reddish-brown needles, which is comparatively easily hydrolysed by water and forms with cold dilute sodium hydroxide a dark blue *substance*, probably the base in the form of a quinol or quinhydrone.

β-Orcinolphthalein is much more prone than the α-isomeride to form oxonium salts, even 10% hydrochloric acid producing an orange-red chloride. By boiling with methyl alcoholic hydrogen chloride, β-orcinolphthalein yields the *methyl ester oxonium chloride*,

$$OCl{<}\begin{matrix}C_6H_2Me(OH)\\C_6H_2Me(OH)\end{matrix}{>}C{\cdot}C_6H_4{\cdot}CO_2Me,$$

brick-red needles, whilst by treatment with methyl iodide and aqueous sodium hydroxide it yields *β-orcinolphthalein dimethyl ether*,

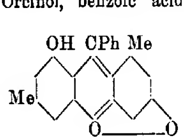
$$O{<}\begin{matrix}C_6H_2Me(OMe)\\C_6H_2Me(OMe)\end{matrix}{>}C{<}\begin{matrix}C_6H_4\\O\end{matrix}{>}CO,$$

m. p. 247—250°, colourless crystals, which like the dimethylated α-isomeride has little tendency to the formation of stable oxonium salts. The dimethyl ether and methyl alcoholic hydrogen chloride yield the *oxonium chloride*, $OCl{<}\begin{matrix}C_6H_2Me(OMe)\\C_6H_2Me(OMe)\end{matrix}{>}C{\cdot}C_6H_4{\cdot}CO_2Me$, tufts of yellowish-red needles, which dissolves in cold water without hydrolysis, forming an intensely bitter, orange-yellow solution. The solution is attacked only slowly by sodium acetate or sodium hydrogen carbonate, more rapidly by alkali carbonates or hydroxides, yielding the colourless *carbinol*, from which, immediately after its formation, the orange-yellow salts can be regenerated; the *platinichloride* and *nitrate* are described.

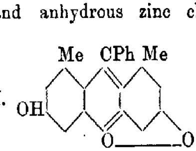
γ-Orcinolphthalein, which is readily freed from its isomerides by means of methyl-alcoholic hydrogen chloride, whereby the pure *chloride* is precipitated in orange-yellow leaflets with a blue shimmer, is not readily etherified or esterified.

Orcinol, benzoic acid, and anhydrous zinc chloride heated at 160—170° for six to seven hours yield a mixture of *β-orcinolbenzein*, (formula I), orange-red crystals, m. p. 260—265°, and *γ-orcinolbenzein* (formula II), orange-red crystals with a bluish shimmer, m. p. about 270°, the former being isolated as the *alcoholate*, colourless prisms. A concentrated alcoholic solution of this alcoholate and concentrated hydrochloric acid yield, after short boiling, the *oxonium chloride*, $C_{21}H_{17}O_3Cl$, red crystals with a violet shimmer. α-Orcinolbenzein has not been isolated.

I.



II.



By heating with aqueous sodium hydroxide and methyl iodide, β-orcinolbenzein yields the *dimethyl ether*, $C_{23}H_{22}O_4$, m. p. 192—193°,

colourless crystals, which is probably the carbinol,

$$OMe\cdot C_6H_2Me\underset{O}{\overset{CPh(OH)}{<\!\!\!=\!\!\!>}}C_6H_2Me\cdot OMe.$$

C. S.

Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], 86, 472—516).—A continuation of previous work (A., 1912, i, 376).

I. *Fluorescein.*—In this section the author gives further details concerning the various modifications of fluorescein, together with an account of the alkali salts of fluorescein and a discussion of their constitution.

Of the five unimolecular yellow varieties of fluorescein, the β- and δ-forms are undoubtedly single chemical individuals, although this may not be the case with the α- and γ-modifications. β-Fluorescein is readily obtained from ordinary fluorescein by boiling (1) with alcoholic hydrogen chloride, (2) with methyl alcoholic potassium hydroxide, and extracting the solution with ether, after acidification with acetic acid. It separates from ether in crystals of the composition $C_{20}H_{12}O_5,C_4H_{10}O$, and on crystallisation from ethyl acetate yields glistening, red leaflets of the βII form, $C_{20}H_{12}O_5$, which becomes red at 280—290° and has m. p. 347°.

A *monosodium* salt of fluorescein having the composition

$$2C_{20}H_{11}O_5Na,2MeOH,H_2O$$

is produced by dissolving fluorescein in methyl-alcoholic sodium hydroxide. It crystallises in lustrous, reddish-yellow leaflets, and when heated increases enormously in volume, after the manner of Pharoah's serpents; the *monopotassium* salt, $C_{20}H_{11}O_5K,MeOH$, prepared in a similar manner, also forms reddish-yellow leaflets.

An anhydrous and alcohol-free *monosodium* salt, $C_{20}H_{13}O_6Na$, is obtained in brownish-red crystals, having a violet lustre, by heating the disodium salt of fluorescein at 220—240°, and subsequently extracting with cold water or hot alcohol; the aqueous or alcoholic extract contains δ-fluorescein, which forms with alcohol, crystals of the composition $4C_{20}H_{12}O_5,EtOH$.

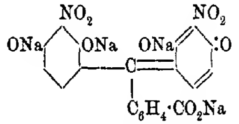
The monosodium salt containing alcohol is at once decomposed by cold water into β-fluorescein and the disodium salt, whilst the alcohol-free salt is insoluble. Further, the anhydrous salt differs from the one containing alcohol in being stable towards cold mineral acids and in yielding a dark brownish-red *sulphate*, $2C_{20}H_{12}O_5,H_2SO_4$, crystallising in leaflets, when boiled with dilute sulphuric acid; the sodium salt containing alcohol yields a *sulphate* of the same composition, but crystallising in yellow leaflets.

A marked difference in the behaviour of the mono- and di-alkali salts of fluorescein has also been observed; the monoalkali salts dissolve in excess of alkali, yielding solutions from which β-fluorescein is liberated by acids, whilst the dialkali salts when subjected to the same treatment give the red variety of fluorescein.

The preparation of a *fluorescein hydrate*, $2C_{20}H_{12}O_5,H_2O$, from the yellow monosodium salt by the action of water is also described; this forms lustrous, light- to violet-red needles, which readily lose their water at the ordinary temperature and then have m. p. 347°.

II. 4:5-*Dinitrofluorescein* (compare Hewitt and Perkins, T., 1900,

77, 1324; Baeyer, A., 1910, i, 249).—The blue tetrapotassium salt of 4:5-dinitrofluorescein, which the author considers to be a *p*-quinonoid salt of the annexed formula, is obtained by dissolving dinitrofluorescein in aqueous alcoholic potassium hydroxide; it forms bluish-violet needles of the composition



$$C_{20}H_6O_5(NO_2)_2K_4,H_2O,EtOH,$$

and yields blue aqueous solutions, which gradually become light red on dilution, owing to hydrolysis and the formation of a red mono- or di-potassium salt. The light red solutions slowly acquire a yellow colour, a change referred by the author to the loss of water and re-formation of the pyrone ring. The rupture of the ring in these yellow solutions may be effected by alkali hydroxides, but not by sodium carbonate or ammonia.

The *hydrate* of 4:5-dinitrofluorescein, $C_{20}H_{10}O_5(NO_2)_2,H_2O$, prepared by acidifying a fresh aqueous solution of the tetrapotassium salt, crystallises from alcohol in red prisms, m. p. 211—212°.

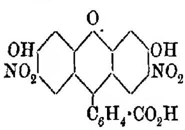
The *ammonium* salt, $C_{20}H_8O_5(NO_2)_2,2NH_3,H_2O,MeOH$, crystallises in large dark red prisims, m. p. 234° (decomp.); it is obtained by dissolving the dinitrofluorescein in methyl-alcoholic ammonia.

When prepared by the action of potassium hydroxide on 4:5-dinitrofluorescein in aqueous solution, the *dipotassium* salt,

$$C_{20}H_8O_5(NO_2)_2K_2,$$

forms a blackish-red mass of a greenish lustre; in alcoholic solution red crystals of the composition $C_{20}H_8O_5(NO_2)_2K_2,H_2O,EtOH$ are obtained.

Addition of strong aqueous ammonia to 4:5-dinitrofluorescein gives rise to the ammonium salt of the acridine compound described by Reverdin (A., 1897, i, 226); this crystallises in red needles of the composition $2C_{20}H_{10}O_4(NO_2)_2{:}NH,3NH_3,6H_2O$.



For the purpose of comparison, 2:7-*dinitrofluorescein* (annexed formula) has been prepared and its behaviour towards alkalis studied. It is obtained as a light red, crystalline powder by boiling the nitrate with water, and resembles the parent compound in forming only yellow or red salts, in which the pyrone ring remains intact. The *nitrate*,

$$C_{20}H_{10}O_5(NO_2)_2,HNO_3,H_2O,$$

crystallises in yellow needles, and is formed by the action of hot 30—35% nitric acid on fluorescein.

III. *Fluorescein Ethers* (compare A., 1912, i, 376).—In addition to the previously described colourless diethyl ether of m. p. 181°, the action of ethyl sulphate on the disodium salt of fluorescein at 100° gives rise to a new colourless *diethyl ether*, crystallising in needles or prisms, m. p. 234—235°. This resembles in its general behaviour the ether of m. p. 181°, but differs from the latter compound in that it does not form oxonium salts and does not undergo reduction in acid solution. A similar difference is shown by the colourless dimethyl ethers of m. p. 255° and 197° (*loc. cit.*); in both cases the behaviour of the ethers of higher m. p. is in better agreement with the

formula $O<\genfrac{}{}{0pt}{}{C_6H_3(OR)}{C_6H_3(OR)}>C<\genfrac{}{}{0pt}{}{-O-}{C_6H_4}>CO$ than that of the less fusible ethers, to which, however, this formula has already been assigned.

By hydrolysing the coloured dimethyl ether of m. p. 208° with aqueous sodium hydroxide, Fischer and Hepp (A., 1895, i, 291) obtained a coloured monomethyl ether of m. p. 262°, which closely resembles the monomethyl ether (m. p. 265°) isolated by the author (*loc. cit.*). When hydrolysed with alcoholic potassium hydroxide the dimethyl ether of m. p. 208° yields a colourless *monomethyl ether*, which probably has the constitution $O<\genfrac{}{}{0pt}{}{C_6H_3(OMe)}{C_6H_3(OH)}>C<\genfrac{}{}{0pt}{}{-O-}{C_6H_4}>CO$. This separates from ethyl acetate in feathery crystals, m. p. 256—257°, forms a dark red *sodium* salt, $C_{21}H_{11}O_5Na$, and on reduction with zinc and glacial acetic acid yields a *substance*, $C_{21}H_{16}O_5$, crystallising in needles, m. p. 205—206°.

The above-mentioned sodium salt corresponds to a *monomethyl ether* of m. p. 266°, which crystallises in lustrous, yellow needles, and is formed by the action of methyl sulphate on an aqueous solution of the disodium salt of fluorescein.

The monomethyl ether of m. p. 265° (or 262°) forms a *sodium* salt of the composition $C_{42}H_{32}O_{14}Na_3$, whilst a coloured *monomethyl ether*, obtained in yellowish-white crystals, m. p. 272°, by methylating fluorescein with methyl iodide and potassium hydroxide in alcoholic solution, yields a blackish-red *sodium* salt having the composition $C_{21}H_{12}O_5Na_2,H_2O$. Since the monomethyl ethers of m. p. 262°, 265°, and 272° do not yield monosodium salts, the conclusion is drawn that these compounds cannot be represented by the formula $O<\genfrac{}{}{0pt}{}{C_6H_4(OMe)}{-C_6H_3(:O)}\geqslant C\cdot C_6H_4\cdot CO_2H$. When warmed with alcohol and hydrochloric acid and the resulting *chloride* heated at 250°, the dimethyl ether of m. p. 208° yields a small amount of the dimethyl ether of m. p. 197°. The latter compound was also obtained in an attempt to prepare a trimethyl ether of fluorescein by the oxidation of the corresponding ether of fluorescin with lead dioxide in glacial acetic acid solution.

Fluorescin trimethyl ether, $C_{23}H_{20}O_5$, prepared by warming fluorescin with strong aqueous potassium hydroxide and methyl sulphate, crystallises in small prisms or leaflets, m. p. 136°. It is accompanied by a *fluorescin monomethyl ether*, $C_{21}H_{16}O_5$, which separates with benzene (1 mol.) in crystals of m. p. 120—125°; in one instance a *substance* was obtained, which crystallised in leaflets, m. p. 204°, and resembled in its behaviour the reduction product of the dimethyl ether of m. p. 197°, mentioned below.

In addition to the dimethyl ethers of m. p. 197°, 208° and 255°, and the monomethyl ether of m. p. 266°, the action of methyl sulphate on an aqueous solution of the disodium salt of fluorescein yields the following substances: (1) a quadrimolecular *monomethyl ether*, $3C_{20}H_{12}O_5,C_{21}H_{14}O_5$, which separates from a mixture of benzene and alcohol in red or brownish-yellow crystals, which become red at 260°, or in crystals containing 4EtOH; all three modifications have m. p. 330—333°. (2) A *monomethyl* ester, $O<\genfrac{}{}{0pt}{}{C_6H_3(OH)}{-C_6H_3(:O)}\geqslant C\cdot C_6H_4\cdot CO_2Me$, which forms

dark red crystals of a violet lustre, m. p. 282—283°. (3) A *hydrate* of the above ester, $C_{21}H_{14}O_3,H_2O$, crystallising in yellow needles, which become red and melt at 280°.

The monomethyl ester, m. p. 282—283°, is also formed by directly esterifying fluorescein with alcohol and hydrogen chloride, whilst esterification with alcohol and sulphuric acid gives rise to a monomethyl ester of m. p. 252° (compare Feuerstein and Wallach, A., 1901, i, 723).

Methylation of fluorescein by means of methyl iodide and alcoholic potassium hydroxide yields the monomethyl ethers of m. p. 256—257°, 265° and 272°, the dimethyl ether, m. p. 208°, and the quadrimolecular monomethyl ether of m. p. 330—333°.

The *hydrochloride* of the monomethyl ester of m. p. 282—283°, $C_{21}H_{14}O_5,HCl$, forms orange-yellow needles (decomp. 260°).

The monomethyl ether of m. p. 272° yields a *hydrochloride*,

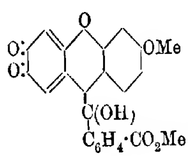
$$3C_{21}H_{14}O_5,2HCl,4H_2O,$$

crystallising in brownish-yellow needles, m. p. 250°.

The products obtained by reducing the ethers of fluorescein, containing a free carboxyl group, with zinc and glacial acetic acid form crystalline compounds with benzene, which is firmly retained until about 110°, whilst those obtained from ethers in which the carboxyl group has been esterified or undergone lactone formation readily lose their benzene below 100°.

The *substance*, $C_{21}H_{16}O_5$, obtained by reducing the monomethyl ether of m. p. 257°, forms needles, m. p. 205—206°; that from the monomethyl ether of m. p. 266° separates in crystals, which become yellow and lose their benzene at 120—125°. The monomethyl ether of m. p. 265° yields a *substance*, $C_{21}H_{16}O_5,2C_6H_6$, which has m. p. 132—133° or 169—170° accordingly as it is dried at 100° or 140°. The *substance* from the monomethyl ether of m. p. 272° has m. p. 173—174°, that from the monomethyl ester of m. p. 282° separates from alcohol in small needles of the composition $C_{21}H_{16}O_5,EtOH$, m. p. 190—191°, and from benzene in crystals which melt at 83—84°, solidifies at a higher temperature, and then melts at 190—191°. The quadrimolecular monomethyl ether on reduction yields a *substance*, $3C_{20}H_{14}O_5,C_{21}H_{16}O_5,H_2O,8C_6H_6$, which loses benzene below 100°, sinters at 220°, and melts at 237—238°.

The *substance*, $C_{22}H_{18}O_5$, obtained from the dimethyl ether of m. p. 197°, forms clusters of needles, m. p. 204°; that from the dimethyl ether of m. p. 208°, stout crystals, m. p. 165°. When oxidised with lead dioxide or hydrogen peroxide in acetic acid solution the last-mentioned reduction product yields a dark red *substance* (decomp. about 200°), which forms dark brown alkali salts, and is probably produced by the oxidation of one of the resorcinol residues, as shown in the annexed formula.

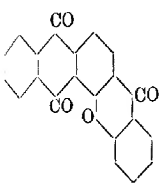


The author suggests that the above results are best explained on the assumption that the ordinary red fluorescein is a polymeride, consisting probably of various di-, ter-, and quadri-molecular combinations as in the case

of resorcinolbenzein, and that the methyl ether of m. p. 330—333°, containing one methyl group to four fluorescein molecules, represents the initial stage in the methylation of the quadrimolecular form, the further methylation resulting in a more or less complete degradation into simple molecules. F. B.

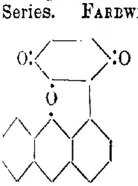
Preparation of Xanthones of the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251696).—Xanthones of the anthraquinone series are readily prepared by the action of condensing agents on phenyl, naphthyl, or anthraquinonyl ethers of 1-hydroxyanthraquinone-2-carboxylic acids or their substituted derivatives.

1-*Phenoxyanthraquinone-2-carboxylic acid*, tablets, m. p. 272°, is prepared by the fusion of 1-chloroanthraquinone-2-carboxylic acid (10 parts) with phenol (60 parts) and potassium hydroxide (25 parts) during four hours at 150°. When this product, suspended in trichlorobenzene, is treated with phosphorus pentachloride and the temperature slowly raised, it furnishes the *xanthone* (annexed formula), which separates in yellow, glistening tablets.



1-*Naphthoxyanthraquinone-2-carboxylic acid*, yellow tablets, m. p. 262°, is prepared in a similar manner from β-naphthol at 130—140° during two hours; the corresponding *xanthone* is obtained as greenish-yellow leaflets, m. p. above 300°; it dissolves in alkaline hyposulphite with an intense blue, and in concentrated sulphuric acid with a brownish-red, coloration. F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251020).—The *compound*, $C_{20}H_{10}O_3$ (annexed formula), a black powder, is obtained when anthranol and *p*-benzoquinone are boiled together in nitrobenzene solution; it dissolves in concentrated sulphuric acid with a violet-red coloration.



The tinctorial properties of other analogous compounds obtained from *p*-benzoquinone with substituted anthranols are tabulated in the original. F. M. G. M.

Preparation of "7:7′-Diaminothioindigo." FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 252771).—When "7:7′-dinitrothioindigo" (or its substituted derivatives) is reduced with sodium sulphide or dextrose it yields the corresponding "7:7′-diaminothioindigo," a black powder, whilst "5:5′-dichloro-7:7′-dinitrothioindigo" furnishes "*5:5′-dichloro-7:7′-diaminothioindigo*," also a black powder. F. M. G. M.

Carpiline, a New Alkaloid from Jaborandi. ÉMILE LÉGER and FERDINAND ROQUES (*Compt. rend.*, 1912, 155, 1088—1091*).—An

* and *J. Pharm. Chim.*, 1913, [vii], 7, 5—13.

extract of *Pilcarpus microphyllus*, after the removal of the greater portion of the bases as their hydrochlorides, yields, on precipitating from the mother liquor, the alkaloid *pilocarpiline*, $C_{16}H_{18}O_3N_2$, m. p. 184—185°, α_D +24°. It is soluble in chloroform, benzene, and boiling water, and crystallises in colourless prisms. It is a feeble base, its salts with organic acids being dissociated by alcohol, whilst those with mineral acids are stable, all having a bitter taste. It gives a *hydrochloride*, $C_{16}H_{18}O_3N_2,HCl$, colourless prisms; a *sulphate*; a *platinichloride*, $(C_{16}H_{18}O_3N_2)_2,H_2PtCl_6,5H_2O$, crystalline plates, and a *methiodide*, $C_{16}H_{18}O_3N_2,MeI$, small, pale yellow prisms. The base is saturated, since its salts do not reduce potassium permanganate in the cold.

Carpiline contains a lactone group, and thus dissolves in alkali hydroxide solutions, giving compounds of the type *potassium carpilinate*, $C_{12}H_{19}O_4N_2K$, long needles, very soluble in water. The presence of an hydroxyl group is shown by the formation of an amorphous benzoyl derivative which yields *benzoylcarpiline platinichloride*,

$$[C_{16}H_{17}O_3N_2Bz]_2,H_2PtCl_6.$$

The alkaloid on oxidation with nitric acid yields benzoic acid, and on heating with water at 140° in a sealed tube, it is decomposed, giving benzaldehyde and two amorphous bases, but no hydrogen cyanide. The alkaloid thus contains the groups CHPh:, –OH, $\begin{matrix}-CO\\ | \\ -O\end{matrix}$, and the group $C_8H_{11}N_2$, the constitution of which has yet to be elucidated. Carpiline is but slightly toxic, and has not the same effect as pilocarpine on the secretions. W. G.

Active Principles of Catha Edulis. RALPH STOCKMAN (*Pharm. J.*, 1912, 89, 676—678).—The leaves and twigs of this plant have long been used in Abyssinia, Somaliland, and Arabia as a stimulant-narcotic. They are now shown to contain at least three alkaloids, cathine, cathidine, and cathinine, to which the characteristic physiological action of the plant is due. By mixing a dry aqueous extract of the plant with slaked lime and extracting with dry alcohol, 0·65 and 0·75% of amorphous alkaloids are obtained from the leaves and twigs respectively. This amorphous mixture appears to consist largely of cathine and its alteration products, but no crystalline alkaloid could be isolated from it. The finely-powdered leaves were extracted completely with cold water or very dilute sulphuric or lactic acid, and the liquor made alkaline and extracted with chloroform, which removed cathine along with much impurity, from which the alkaloid was eventually separated as the sulphate. The ground, partly extracted leaves were then mixed with aqueous sodium carbonate and extracted with ether, which removed cathidine and cathinine; these were separated by taking advantage of the fact that the former is precipitated by sodium carbonate solution from aqueous solutions of its hydrochloride, whilst cathinine remains in solution along with some cathidine.

Cathine sulphate crystallises in colourless needles, is neutral in reaction, has a bitter taste, is precipitated by iodine solution, Mayer's reagent or picric acid, but not by tannin or platinic chloride. *Cathine* crystallises from chloroform and appears to be unstable in presence of

alkalis. Its physiological action on the nervous and muscular systems of the frog is similar to those exerted by morphine and caffeine; in large doses it paralyses the terminations of the motor nerves.

Cathidine is colourless and amorphous and has a bitter taste; it gives precipitates with the usual alkaloidal reagents. Cathidine is a muscle poison, and a slight stimulant to the nervous system.

Cathinine sulphate crystallises from water in rosettes of needles, has a bitter taste, and is precipitated by the usual alkaloidal reagents. The free base has only been obtained as a gummy or semi-crystalline mass. Cathinine is less depressant than cathine in its action on the brain, but has a greater stimulant effect on the spinal cord; it paralyses the terminations of the motor nerves.

All three alkaloids in mammals and man act chiefly on the cerebrum and spinal cord, causing stimulation or much excitement according to the dose; cathine produces drowsiness at first. The leaves also contain a fermentable sugar, tannin, caoutchouc, wax, and volatile oil.

T. A. H.

Preparation of Esters of Hydroquinine. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 251936. Compare A., 1912, i, 1013).—It is found that the hydroquinine esters described previously can be most easily prepared in the presence of either finely divided metals of the platinum group or their colloidal solutions.

Hydroquinine ethyl carbonate (*loc. cit.*) is obtained when quinine ethyl carbonate (10 parts), 20% sulphuric acid (14 parts), and 80 parts of water are shaken with 0·1 part of colloidal palladium in 10 parts of water in an atmosphere of hydrogen under pressure until no further absorption of hydrogen is observed; ammonium hydroxide is added, and the product extracted with ether.

Acetylhydroquinine, large, colourless crystals, m. p. 100°, is prepared in a similar way from acetylquinine, and *p*-aminobenzoylhydroquinine (*loc. cit.*) is also described.

F. M. G. M.

Preparation of Esters of Hydrogenised Cinchona Alkaloids. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 253357. Compare A., 1912, i, 1013, and preceding abstract).—The following esters are of therapeutic value.

Hydrocinchonine ethyl carbonate, colourless, tasteless needles, m. p. 134°, is obtained when cinchonine ethyl carbonate (30 parts) dissolved in 160 parts of alcohol is shaken with 1 part of colloidal palladium in 60 parts of water until the absorption of hydrogen ceases.

Benzoylhydrocupreine, colourless crystals, m. p. 172°, is prepared from hydrocupreine.

Dibenzoylhydrocupreine, needles, has m. p. 147°, whilst *ethylhydrocupreine ethyl carbonate* is obtained from ethylhydrocupreine and ethyl chloroformate in benzene solution; it is conveniently isolated in the form of its *salicylate*, colourless crystals, m. p. 138—142°.

F. M. G. M.

Physostigmine [Eserine]. FRANZ EISSLER (*Biochem. Zeitsch.*, 1912, 46, 502).—Eserine gives with diazotised sulphanilic acid in alkaline solution a red colour, which indicates the presence of a pyrrole ring.

This result is in accordance with the recent investigations of Salway (T., 1912, 101, 978). S. B. S.

d-Lupanine. August Beckel (*Arch. Pharm.*, 1912, 250, 691—710. Compare A., 1911, i, 743).—In continuation of previous work, the oxidation of *d*-lupanine by various agents has been investigated, and the products obtained are described.

Chromic acid in large excess oxidises lupanine to a substance containing two additional oxygen atoms, but this was produced in too small quantity to be isolated. Hydrogen peroxide gives rise to two products: the first of these gives an *aurichloride*, m. p. 214°, crystallising in needles, and the other an *aurichloride*, m. p. 188—189°, and *platinichloride*, m. p. 222—227°, crystallising in rosettes of needles. Analyses of these double salts indicate that both oxidation products have the formula $C_{15}H_{24}O_2N_2$. Potassium permanganate in presence of sodium carbonate oxidises lupanine to a *product*, $C_{15}H_{24}O_3N_2$, which was isolated as the *aurichloride*, m. p. 188—189°, and converted into the *platinichloride*, $B_2,H_2PtCl_6,2H_2O$, m. p. 219—221° (decomp.), crystallising in needles.

In the action of bromine on lupanine no fission occurs, as has been suggested by previous workers (Callsen, A., 1900, i, 186; Soldaini, A., 1905, i, 371). A perbromide of the alkaloid is first formed, and this on warming with alcohol may give rise to several different products, depending on the conditions observed. In the present series of experiments, three products melting at 228—236°, 190—210°, and 186—188° respectively were obtained. The first of these consists essentially of *ethoxylupanine dihydrobromide*, $C_{15}H_{23}ON_2\cdot OEt,2HBr$, m. p. 227—228°, $[\alpha]_D^{17-23}$ $-129\cdot4°$, which crystallises in colourless, slender needles from boiling alcohol, and is apparently the "substance, $C_8H_{15}ON,HBr$," described by previous workers. The specific rotation falls, slowly in the cold, more rapidly on warming, when this substance is dissolved in hydrobromic acid, but returns to its normal value when the solution is mixed with alcohol and evaporated to dryness. In presence of excess of alkali the alkaloid is dextrorotatory. The *dihydriodide*, m. p. 221—222°, forms colourless needles; the *dithiocyanate*, $C_{15}H_{23}ON_2\cdot OEt,2HSCN,H_2O$, m. p. 172—174°, crystallises from water in colourless needles, and becomes anhydrous at 100°. The *aurichloride*, $(C_{15}H_{23}ON_2\cdot OEt)_2,4HCl,3AuCl_3$, m. p. 145—150°, crystallises in small, yellow leaflets, and on warming in dilute hydrochloric acid gives *hydroxylupanine aurichloride*,

$$(C_{15}H_{23}ON_2\cdot OH)_2,4HCl,3AuCl_3,$$

which sinters at 122—123°, and crystallises badly in leaflets. Ethoxylupanine does not readily reduce permanganate. Hydriodic acid converts it into a substance which was isolated as the methiodide; the latter resembles lupanine methiodide in rotation, crystalline form, and melting point, but on treatment with silver chloride and gold chloride yields an *aurichloride*, $(C_{15}H_{24}ON_2,MeCl,AuCl_3)_2,HAuCl_4$, m. p. 210°, crystallising in leaflets, whilst the aurichloride obtained in like manner from lupanine methiodide has the composition

$$C_{15}H_{24}ON_2,MeCl,AuCl_3,$$

and melts at 200—205°. The *platinichloride*, m. p. 224—226°,

crystallises in slender, brown needles, and is also abnormal in composition.

The second oxidation product, m. p. 190—210°, contained some ethoxylupanine dihydrobromide, and after the removal of this formed a crystalline mass, m. p. 192—194°, which was probably a mixture of hydrobromides.

The third product, m. p. 186—188°, on recrystallisation from boiling alcohol gave what seems to be a mixture of ethoxylupanine dihydrobromide with either hydroxylupanine hydrobromide or lupanine dihydrobromide, whilst from the mother liquor d-*lupanine dihydrobromide*, B,2HBr,H_2O, m. p. 188—189°, $[\alpha]_D + 45.9°$, was isolated.

T. A. H.

Morphineglucoside. CARL MANNICH (*Annalen*, 1912, **394**, 223—228).—Morphine in $N/2$-sodium hydroxide is shaken for six hours with ethereal β-acetylbromoglucose. The ethereal solution is shaken with 1% hydrochloric acid. The acid extract, by treatment with ammonia, yields *morphinetetra-acetylglucoside*,

$$C_{17}H_{18}O_3N \cdot C_6H_7O_5Ac_4, H_2O,$$

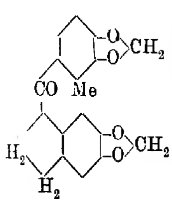
m. p. 154—156°, colourless needles (*hydrochloride*, m. p. about 220° [decomp.]). By hydrolysis with $N/2$-alcoholic potassium hydroxide, the substance yields *morphineglucoside*, $C_{17}H_{18}O_3N \cdot C_6H_{11}O_5, H_2O$, m. p. 183—193°, fine needles. The glucoside, which is more conveniently obtained by the interaction of morphine, $N/2$-sodium hydroxide, and acetylbromoglucose in aqueous acetone and hydrolysis of the product, does not reduce boiling Fehling's solution, and yields dextrose and morphine by hydrolysis with $N/2$-hydrochloric acid on the water-bath.

C. S.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.*, 1912, **250**, 684—691. Compare A., 1899, i, 92; 1907, i, 79; 1911, i, 913, and Faltis, A., 1912, i, 796).—A reply to Faltis (*loc. cit.*) criticising his results and suggesting, as the result of new analyses, that the bebeerines are better represented by the formula $C_{17}H_{19}O_3N$ than by those previously suggested by the author and by Faltis.

T. A. H.

Protopine and Cryptopine. PETER W. DANCKWORTT (*Arch Pharm.*, 1912, **250**, 590—646).—A résumé of previous papers relating to the distribution of protopine in the natural orders, *Papaveraceae* and *Fumariaceae*, and its characters and chemistry is first given. It is then shown by analogy with other papaveraceous alkaloids that protopine probably contains an *iso*quinoline group, and evidence is brought forward for the view that it contains two methylenedioxy-groups and a carbonyl group, and that the nitrogen atom has a $\cdot CH_3$ group attached to it. On these and other grounds the annexed formula is assigned provisionally to the alkaloid.



Dicentra (*Diclytra*) *spectabilis* tubers yielded 0.65% of crude alkaloid, chiefly protopine. The latter has the formula $C_{20}H_{19}O_5N$, and crystallises from a mixture of chloroform and alcohol

in colourless prisms or from ether in nodular masses: both forms melt at 207°, but the first gives with sulphuric acid a yellow coloration changing to blue, reddish-violet, and green, and with Fröhde's reagent a yellowish-olive colour changing to dirty violet, green, blue, and finally green; the second form, on the contrary, with sulphuric acid gives a deep yellow, passing into green, dirty reddish-brown, and finally green, whilst with Fröhde's reagent it yields a yellowish-olive solution which becomes violet and finally green.

Protopine contains no hydroxyl groups or methoxyl groups, but gives Gaebel's test for dioxymethylene (A., 1910, i, 501), and the presence of the latter is confirmed by the fact that protopine, when heated under pressure with dilute sulphuric acid, yields a product giving the colour reactions of a catechol derivative. No direct evidence of the presence of a carbonyl group could be obtained. The occurrence of a $\vdots NCH_3$ group was proved by Herzig and Meyer's method. The alkaloid is not reduced by aqueous colloidal platinum, but sodium amalgam in dilute acid converts it into *hydroprotopine*, $C_{20}H_{21}O_5N,\frac{1}{2}EtOH$, m. p. 120° (approx.) or 151—152° (dry), which crystallises from a mixture of ether and alcohol, becomes anhydrous at 100°, is easily soluble in chloroform or ethyl acetate, sparingly in alcohol and slightly in ether; the *hydrochloride* crystallises from alcohol in needles and from water in plates. On treatment with benzoyl chloride hydroprotopine is apparently first benzoylated and then partly converted by loss of H_2O into a *quaternary base*, $C_{20}H_{19}O_4N$, which has not been obtained free from the benzoylated product; it yields a *hydrochloride*, $C_{20}H_{19}O_4N,HCl,5H_2O$, m. p. 275° (approx. decomp.), which is crystalline and from which an *aurichloride*, $B,HAuCl_4$, crystallising in reddish-brown needles is obtainable; this hydrochloride on heating with sodium hydroxide in alcohol is converted into an isomeric *tertiary anhydro-base*, $C_{20}H_{19}O_4N$, m. p. 145°, crystallising in long needles. Both the quaternary and the tertiary anhydro-bases can be prepared in other ways from protopine and hydroprotopine; it is believed that this series of changes from protopine to the tertiary anhydro-base takes place in the following way: $\cdot NMe\cdot\dot{C}H\cdot CO\cdot \longrightarrow \cdot NMe\cdot\dot{C}H\cdot CH(OH)\cdot \longrightarrow$
$\cdot(HCl)NMe\cdot CH\cdot CH(OBz)\cdot \longrightarrow$

$$\cdot ClNMe\vdots C\cdot CH_2\cdot \rightleftarrows \cdot(HO)NMe\vdots CH\cdot CH_2\cdot \leftrightarrows \cdot NMe\cdot C\vdots CH\cdot,$$

the compound represented by the fourth formula being the "hydrochloride" of the quaternary base, and that by the sixth formula being the tertiary anhydro-base.

Methyl iodide converts protopine into the methiodide, whilst methyl sulphate transforms it into *methylprotopine methosulphate*, $C_{20}H_{19}O_5NMe\cdot SO_4Me$, which crystallises from dilute alcohol: either of these substances on heating with alkalis yields *protopinemethine*, $C_{20}H_{18}O_5NMe$, m. p. 136—137°, crystallising in pearly leaflets, which in turn furnishes a crystalline *methiodide*; this on heating with alkali hydroxides in methyl alcohol yields trimethylamine and an amorphous product.

The tertiary anhydro-base also yields a crystalline *methiodide*, m. p. 230°, and a crystalline *methine* base, m. p. 112°, which fluoresces

in ether solutions and gives a bromine additive product. The *methine-methiodide*, rosettes of needles, is not decomposed on heating with alkalis in methyl alcohol, but on treating the methine base with methyl sulphate and heating the product with sodium hydroxide in methyl alcohol an amine is evolved and a resinous vinyl derivative is formed.

Oxidation experiments with protopine and its derivatives did not afford useful results, except in the case of protopinemethine, which on treatment with potassium permanganate in acetone solution yielded a basic substance and hydrastic acid (4:5-methylenedioxy-phthalic acid).

Cryptopine resembles protopine in its solubilities, and in physiological action, and like it contains no hydroxyl group and gives no oxime. Cryptopine contains a methylenedioxy-group, and two methoxyl groups. On reduction with sodium amalgam in dilute sulphuric acid it yields *hydrocryptopine*, m. p. 182—183°, which crystallises from ether and on treatment with benzoyl chloride gives the *hydrochloride* of a *quaternary base*. In view of this it seems likely that cryptopine differs from protopine only in containing two methoxyl groups in place of one methylenedioxy-group, but it is not clear which of the two methylenedioxy-groups of protopine is thus replaced (compare Pictet and Kramers, A., 1910, i, 502, and Brown and Perkin, P., 1891, 7, 161). T. A. H.

Preparation of Acyl Derivatives of Theobromine. KNOLL & Co. (D.R.-P. 252641).—*Acetyltheobromine*, colourless, odourless needles with a bitter taste and m. p. 165°, is obtained by the action of acetyl chloride on a solution of sodium theobromine in chloroform or xylene.

Benzoyltheobromine forms colourless, odourless, tasteless needles, m. p. 206° (about), and is most satisfactorily prepared from silver theobromine and benzoyl chloride in toluene solution.

These compounds are of therapeutic value, and analysis indicates that they are monoacyl derivatives. F. M. G. M.

The Chemical Constitution of Sparteine. CHARLES MOUREU and AMAND VALEUR (*Ann. Chim. Phys.*, 1912, [viii], 27, 245—391).—A résumé of work already published (compare A., 1903, i, 717; 1904, i, 187; 1905, i, 608, 609, 659, 716; 1908, i, 43, 44, 103, 206, 563; 1911, i, 319, 562; 1912, i, 210, 296). W. G.

Some New Sparteine Salts. LOUIS CORRIEZ (*Chem. Zentr.*, 1912, ii, 1566; from *Bull. Sci. Pharmacol.*, 19, 468—480).—The following salts are described: *Basic hydrobromide*, B,HBr [$B = C_{15}H_{26}N_2$], from the basic sulphate and barium bromide, prismatic crystals, m. p. 236°, $[\alpha]_D$ −16°6′; *di-iodide*, B,2HI + H_2O, m. p. (anhydrous) 225°, $[\alpha]_D$ −16°2′; *normal chlorate*, B,2$HClO_3$, colourless cubes, explodes at 147°, $[\alpha]_D$ −23°12′; *basic chlorate*, B,$HClO_3$, colourless prisms, explodes at 200—205°, $[\alpha]_D$ −16°3′; *normal perchlorate*,

$$B,2HClO_4 + 2H_2O,$$

prisms, m. p. 78°, anhydrous, 265°, explodes over 300°, $[\alpha]_D$ −17°30′;

basic perchlorate, $B,HClO_4$, m. p. 171°, $[\alpha]_D$ in methyl alcohol $-17°6'$, in acetone $-16°3'$; *dichromate*, $B,H_2Cr_2O_7$, orange-yellow prisms, decomposes at 128—129°; *normal salicylate*, $B,2C_7H_6O_3+H_2O$, pale pink prisms, m. p. 78°, $[\alpha]_D$ $-8°42'$. J. C. W.

The Constitution of Sparteine Periodide and Sparteine Perbromide. LOUIS CORRIEZ (*Chem. Zentr.*, 1912, ii, 1826; from *Bull. Sci. Pharmacol.*, 1912, 19, 533—540).—The formation of sparteine periodide by the action of 12% hydrogen peroxide on sparteine di-iodide may be expressed thus: $2C_{15}H_{26}N_2,2HI+O=2C_{15}H_{26}N_2,HI+I_2+H_2O$; $C_{15}H_{26}N_2,HI+I_2=C_{15}H_{26}N_2,HI,I_2$. As it would follow from the latter equation, the periodide also results when sparteine mono- or di-iodide is treated with iodine. *Sparteine perbromide*,

$$C_{15}H_{26}N_2,2HBr,Br_2+H_2O,$$

by the action of bromine on sparteine, both dissolved in fuming hydrobromic acid, forms yellow crystals, m. p. 193°. The formation of this perbromide will show the presence of sparteine in a dilution of 1:10,000. J. C. W.

New α-Methylsparteinium Salts. LOUIS CORRIEZ (*Chem. Zentr.*, 1912, ii, 1826; from *Bull. Sci. Pharmacol.*, 1912, 19, 527—532).—Starting from α-methylsparteinium hydroxide, which is obtained in aqueous solution by the action of moist silver oxide on Moureu's α-sparteine methiodide (A., 1905, i, 608), the following salts have been prepared: *Hydrochloride* of *α-sparteine methochloride*,

$$C_{15}H_{26}N_2MeCl,HCl,3H_2O,$$

transparent, hygroscopic crystals, m. p. 194°, $[\alpha]_D$ $-23°9'$; *hydrobromide* of *α-sparteine methobromide*, $C_{15}H_{26}N_2MeBr,HBr,2H_2O$, m. p. 216°, $[\alpha]_D$ $-19°2'$; *α-methylsparteinium dichromate*,

$$C_{15}H_{26}N_2Me\cdot Cr_2O_7H,H_2O,$$

orange-yellow needles, decomposes at 120°; *α-methylsparteinium perchlorate*, $C_{15}H_{26}N_2Me\cdot ClO_4$, transparent needles, decomposes at 230°; *α-methylsparteinium picrate*, $C_{15}H_{26}N_2Me\cdot C_6H_2O_7N_3$, yellow needles, m. p. 218°. J. C. W.

Pyrrolidonecarboxylic Acid and Polypeptides Derived from It. EMIL ABDERHALDEN and ERICH WURM (*Zeitsch. physiol. Chem.*, 1912, 82, 160—166).—Pyrrolidonecarboxyl chloride interacts with cholesterol in chloroform solution in the absence of moisture, forming *cholesteryl pyrrolidonecarboxylate*, $C_{26}H_{43}\cdot O\cdot CO\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ NH-CO\end{matrix}$. This crystallises in colourless, matted needles, which sinter at 199—203°, m. p. 205°.

dl-*Pyrrolidonecarboxyl*-d-*alanine ester* crystallises in rosettes of needles, m. p. 125·5° (corr.), $[\alpha]_D^{20}$ $-46·42°$.

dl-*Pyrrolidonecarboxyl*-dl-*leucine ester* separates in prisms, m. p. 115—117° (corr.). E. F. A.

Chalkones and Hydrochalkones. III. GUIDO BARGELLINI and E. MARTEGIANI (*Gazzetta*, 1912, 42, ii, 427—432. Compare this vol. i, 59).—The authors have applied the mode of reduction previously

described to compounds analogous to chalkones, but containing pyrrole and furan rings, instead of benzene rings. In all cases only two atoms of hydrogen were added, and the rings were not attacked; the experiments were conducted in alcoholic solution (compare Willstätter and Hatt, A., 1912, i, 545).

2-Cinnamoylpyrrole (compare Ciamician and Dennstedt, A., 1885, 378) is conveniently prepared by keeping a mixture of 2-acetylpyrrole and benzaldehyde in the presence of potassium hydroxide in aqueous-alcoholic solution. The *dihydro*-derivative, $C_{13}H_{13}ON$, forms colourless needles, m. p. 70—71°. It dissolves in concentrated sulphuric acid, giving a colourless solution.

2-mp-*Methylenedioxycinnamoylpyrrole*, $C_{14}H_{11}O_3N$, is obtained by keeping 2-acetylpyrrole and piperonaldehyde in the presence of potassium hydroxide in aqueous-alcoholic solution. It dissolves in concentrated sulphuric acid, giving an intense red coloration. On reduction it yields a *dihydro*-derivative, $C_{14}H_{13}O_3N$, which forms colourless needles, m. p. 84—85°, and dissolves in concentrated sulphuric acid, giving a colourless solution.

Furfurylidenepaenol (compare Courant and von Kostanecki, A., 1907, i, 75) gives a *dihydro*-derivative, $C_{14}H_{14}O_4$, which forms colourless needles, m. p. 72—73°.

2-*Furfurylideneacetylpyrrole*, $C_{11}H_9O_2N$, crystallises in yellow needles, m. p. 130—131°; it dissolves in concentrated sulphuric acid, giving an intense red coloration. Its *dihydro*-derivative, $C_{11}H_{11}O_2N$, crystallises in colourless needles, m. p. 70—71°. R. V. S.

Preparation of 2-Indolecarboxylic Acid and 2:3-Dihydroxyquinoline from Oxal-*o*-toluidic Acid. Indole Syntheses. II. Walter Madelung (*Ber.*, 1912, 45, 3521—3527. Compare A., 1912, i, 499).—The synthesis of indole compounds recently described (*loc. cit.*) fails with the application of formyl derivatives, and so the direct synthesis of indole itself in this way fails. By the use of oxal-*o*-toluidic acid, however, the action proceeds in the normal manner with the formation of the expected indolecarboxylic acid, which by careful distillation can be converted into indole (Weissgerber, A., 1911, i, 155).

Oxal-*o*-toluidic acid is conveniently obtained by heating a mixture of equal quantities of *o*-toluidine and anhydrous oxalic acid for an hour at a temperature not exceeding 130°; the concentrated solution of the toluidine salt of the acid on treatment with the necessary quantity of dilute sulphuric acid gives a thick deposit of the free acid. On evaporating the solvent from an alcoholic solution of sodium ethoxide and potassium oxal-*o*-toluidate and raising the temperature of the resultant intimate mixture to 340—350°, reaction takes place with the formation of two products, one of which can be easily dissolved out with benzene. This substance by m. p. 199—202°, and by its yielding indole on heating was evidently indolecarboxylic acid.

The sparingly soluble constituent, prisms, m. p. 257—258°, gives a *diacetyl* derivative, needles, m. p. 211°, and produces with ferric chloride a bluish-green coloration; it is inappreciably attacked by phosphorus pentachloride even at 140°, the only result being a minute

quantity of a *substance*, m. p. 70—90°. It is highly probable that this second constituent of the mixture produced in the original synthesis is 2 : 3-*dihydroxyquinoline*. This decision is at variance with the published results of Friedländer and Weinberg (A., 1883, 351), who ascribe a considerably higher m. p. and no ferric chloride coloration. A repetition of Friedländer and Weinberg's method of preparation, namely, fusion of 3-chloro-2-hydroxyquinoline with potassium hydroxide, showed that under certain conditions the dihydroxyquinoline, m. p. above 300°, of these investigators becomes a subsidiary product, whilst a by-product mentioned by them becomes the main resultant substance, identical with the author's dihydroxyquinoline. The correctness of this view, that the earlier description of dihydroxyquinoline is a mistake, is confirmed by the action of phosphorus pentachloride, which converts the substance (m. p. above 300°) into a compound which sinters at 102°, decomposes at a higher temperature, and is quite distinct from 2 : 3-dichloroquinoline. D. F. T.

Preparation of Derivatives of 2-Phenylquinoline-4-carboxylic Acid and its Homologues. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 252643).—2-Phenylquinoline-4-carboxylic acid and its homologues, although of therapeutic value, have the disadvantage of a bitter taste; this drawback is absent in the amides which have now been prepared.

The *chloride* of 2-phenylquinoline-4-carboxylic acid is a yellow powder, m. p. 230°, and the *amide*, glistening, colourless, hair-like needles, m. p. 195°; whilst the *amide* of 2-phenyl-6-methylquinoline-4-carboxylic acid forms glistening needles, m. p. 257°.

F. M. G. M.

Salts of Acridine, Pyridine, and Quinoline. Lee H. Cone (*J. Amer. Chem. Soc.*, 1912, **34**, 1695—1706).—The object of this work was to study the analogy between the derivatives of the triphenylcarbinols and xanthenols, on the one hand, and those of the acridols on the other, and to show that this analogy extends to the salts of pyridine and quinoline. It has been found that the haloids of phenylacridol, pyridine, and quinoline react with silver to form silver haloids and unsaturated compounds, similar to triphenylmethyl, which readily absorb oxygen. The ammonium salts, such as phenylbenzyldimethylammonium chloride and tetramethylammonium iodide, do not react in this way. The conclusion is therefore drawn that the salts of acridine, pyridine, and quinoline are probably quinocarbonium salts and not ammonium salts, as has been generally assumed.

When diphenylacridol chloride (Gomberg and Cone, A., 1910, i, 59) is suspended in nitrobenzene and treated with molecular silver, a double *silver* salt, $C_{25}H_{18}NCl,AgCl$, is produced, together with an unsaturated compound which absorbs oxygen to form a peroxide, thus: (1) $C_{25}H_{18}NCl + Ag = C_{25}H_{18}N- + AgCl$; (2) $C_{25}H_{18}NCl + AgCl = C_{25}H_{18}NCl,AgCl$; (3) $2C_{25}H_{18}N- + O_2 = (C_{25}H_{18}N)_2O_2$.

When 5-*phenyl*-10-*methylacridol chloride hydrochloride*,

$$NMe{<}\begin{matrix}C_6H_4(Cl,HCl)\\C_6H_4\end{matrix}{>}CPh,$$

is heated at 90—100° and a current of air passed through it, it is converted into the *chloride*, $NMe<{}^{C_6H_4Cl}_{C_6H_4}>CPh$, which, on being treated with molecular silver, yields a double *silver* salt,

$$C_{20}H_{16}NCl,AgCl,$$

and an unsaturated compound which absorbs oxygen.

If pyridine methyl iodide is shaken with nitrobenzene and excess of silver, a similar reaction occurs with formation of a double iodide and an unsaturated compound which absorbs oxygen. Quinoline methiodide behaves in the same way. E. G.

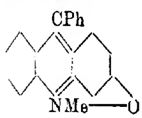
Acridine Derivatives. II. Analogue of *apo*Safranone in the Acridine Series. FRIEDRICH KEHRMANN and ZD. MATUSINSKY (*Ber.*, 1912, **45**, 3498—3505).—2-Hydroxy-5-phenylacridine is best obtained by heating, without stirring, an intimate mixture of *m*-hydroxydiphenylamine, benzoic acid, and zinc chloride at 180—200°, and finally at 210°, for half an hour at each temperature; a crystalline by-product is also obtained, the removal of which presents some difficulty. The hydroxyphenylacridine crystallises from hot saturated solutions in straw-yellow needles, m. p. 264°, and at the ordinary temperature in brick-red prisms, m. p. about 135°, changing to the yellow modification. On the contrary, the yellow form changes to the red by long keeping at the ordinary temperature. The suggestion is offered that the two modifications have an ortho- and a para-quinonoid constitution respectively:

$$C_6H_4<{}^{CPh}_{-N-}>C_6H_3\cdot OH \text{ and } C_6H_4<{}^{CPh}_{NH}>C_6H_3:O.$$

2-*Acetoxy*-5-*phenylacridine*, m. p. 151°, pale-yellow leaflets, reacts with methyl sulphate in nitrobenzene at 140—150° to form 2-*acetoxy*-5-*phenyl*-10-*methylacridinium methosulphate*,

$$CPh<{}^{-C_6H_4-}_{C_6H_3(OAc)}>NMe\cdot SO_4Me,$$

citron-yellow needles, from which a *chloride*, *bromide*, *iodide*, and *platinichloride*, yellow to orange-red, crystalline salts, can be prepared.



By warming a dilute aqueous solution of one of these salts with sodium hydroxide on the water-bath, C-*phenyl*-N-*methyl*iso*acridone* (annexed formula), m. p. 231°, brownish-red or dark red needles, is obtained. This substance sublimes unchanged, does not react with alkalis, but forms with acids crystalline, red and yellow salts which are completely hydrolysed by water. It yields salts of the preceding acetoxyphenylmethylacridinium base by prolonged keeping with acetic anhydride and treatment of the resulting solution with metallic salts, and is converted by methyl sulphate in nitrobenzene at 150° into 2-*methoxy*-5-*phenyl*-10-*methylacridinium methosulphate*, citron-yellow needles, from which the corresponding *chloride*, *iodide*, *platinichloride*, and *dichromate* have been prepared. C. S.

Action of Phthalic Anhydride on Some Pyrrole Derivatives. HANS FISCHER and FR. KROLLPFEIFFER (*Zeitsch. physiol. Chem.*, 1912, **82**, 266—272).—The trisubstituted pyrroles are at

present characterised as picrates or as the azo-dyes formed with diazobenzenesulphonic acid. They also form characteristic crystalline phthalides when heated with phthalic anhydride and acetic acid in sealed tubes at 180—190°.

3-*Acetyl*-2 : 4-*dimethylpyrrolephthalide*,

$$C_6H_4\left\langle\begin{matrix}CO\cdot C\colon CMe\\ \vert \\ CO\cdot N\cdot CMe\end{matrix}\right\rangle C\cdot COMe,$$

crystallises in faintly yellow-coloured needles, m. p. 183°. On heating with potassium hydroxide it is converted into the corresponding *acid*, which crystallises in slender, colourless needles, m. p. 176—178°.

Cryptopyrrolephthalide separates in brownish-yellow needles, m. p. 169°; the corresponding acid has m. p. 195° (decomp.).

Phonopyrrolecarboxylic acid phthalide forms faintly yellow-coloured needles, m. p. 225—226°; it can be prepared easily from syrupy phonopyrrolecarboxylic acid.

Haemopyrrolephthalide forms yellow prisms, m. p. 116°.

Tetramethylpyrrole and phthalic anhydride yield a *trimethylpyrrolephthalide*, crystallising in stunted, yellow prisms, m. p. 205°. The *acid* obtained on heating with potassium hydroxide has m. p. 204° (decomp.). E. F. A.

The Methylation of Gallocyanin, Pyrogallin, and Azurin. FRIEDRICH KEHRMANN and A. BEYER (*Ber.*, 1912, 45, 3338—3345).—The preparation of oxonium salts analogous to those obtained from resorufin (Kehrmann and Vogt, A., 1910, i, 409) offers in the case of the above substances considerably more difficulty.

The starting substances, gallocyanin, its methyl ester, pyrogallin (m. p. 240—241°), and azurin were first carefully purified and their properties re-examined.

Gallocyanin, on methylation in sodium hydroxide solution with methyl sulphate, gave the phenolic *ether*, $O\left\langle\begin{matrix}C_6H(OMe)(CO_2H)\\ \vert\vert \\ O\text{——}C_6H_3(NMe_2)\end{matrix}\right\rangle N$, deep blue powder, m. p. 203—204°, which forms salts with acids and bases; the solution of this substance in fuming sulphuric acid when diluted changes colour from red to blue, and again to red, indicative of the existence of tri-, di-, and mono-acid salts. Simultaneously with the above ether there is obtained *dimethylgallocyanin*,

$$O\left\langle\begin{matrix}C_6H(OMe)(CO_2Me)\\ \vert\vert \\ O\cdot C_6H_3(NMe_2)\text{——}\end{matrix}\right\rangle N,$$

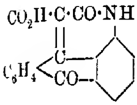
which is better obtained, however, by the action of methyl sulphate on the methyl ester of gallocyanin; it forms prisms with a bronze lustre, m. p. 197°, is insoluble in alkalis, but with acids gives crystalline salts; the solution in fuming sulphuric acid on dilution gives the same series of colour changes as the phenolic ether; *platinichloride*, crystalline.

Methyl sulphate acts on an alkaline solution of pyrogallin, giving a phenolic *ether*, $O\left\langle\begin{matrix}C_6H_2(OMe)\text{==}\\ \vert\vert \\ O\cdot C_6H_3(NMe_2)\end{matrix}\right\rangle N$, prisms with a green lustre, m. p. 199—200°. The solution in fuming sulphuric acid shows the usual colour changes on dilution.

Azurin can be methylated by heating with methyl alcohol containing a little hydrochloric acid, forming the *ester*, $O<\substack{C_6H_2(CO_2Me)= \\ O\cdot C_6H_3(NMe_2)}>N$, prisms with a metallic lustre, m. p. 190°; the solution in concentrated mineral acid changes from a blue to a red colour on dilution.

D. F. T.

Preparation of Anthrapyridonecarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250885).—When the compound, $C_6H_4<\substack{CO\\CO}>C_6H_3\cdot NH\cdot CO\cdot CH_2\cdot CO_2Et$ obtained by heating together molecular proportions of ethylmalonyl chloride and a-aminoanthraquinone at 200° is boiled with aqueous sodium hydroxide it yields *anthrapyridonecarboxylic acid*, $C_{17}H_9O_4N$ (annexed formula); this compound exhibits a yellow fluorescence when dissolved in concentrated sulphuric acid.



The analogous *compound*, $C_{17}H_{10}O_4N_2$, prepared from 1:4-diamino-anthraquinone is a red powder; and the *compound* from 4-chloro-1-aminoanthraquinone an orange-yellow powder.

F. M. G. M.

Preparation of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 252839).—The condensation of aldehydes with *o*-diaminoanthraquinones has been recorded; this action is now found to take place with 1-amino-2-hydroxyanthraquinone or with 1-aminoanthraquinone-2-thiol, yielding compounds of the general formulæ:

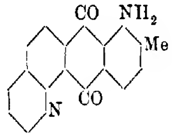
$$A<\substack{NH_2\\OH} \rightarrow A<\substack{N\\O}>CR. \qquad A<\substack{NH_2\\SH} \rightarrow A<\substack{N\\S}>CR.$$

The following *compounds* are described: from benzaldehyde with (1) 1-amino-2:4-dihydroxyanthraquinone, an orange, crystalline powder; (2) with 2:4-diamino-1-hydroxyanthraquinone, brown crystals; (3) with 3-amino-1:2-dihydroxyanthraquinone, orange needles; (4) with 1:5-diamino-2:4:6:8-tetrahydroxyanthraquinone; (5) with 1-aminoanthraquinone-2-thiol; from 1-amino-2:4-dihydroxy-anthraquinone with paraformaldehyde, whilst the *anthra*-1:2-*oxazole* from 1-amino-2-hydroxyanthraquinone forms yellow crystals.

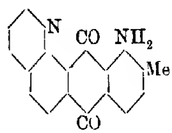
F. M. G. M.

1-Amino-2-methylanthraquinone-a-quinolines. ALFRED SCHAARSCHMIDT and ALEX. STAHLSCHMIDT (*Ber.*, 1912, **45**, 3452—3456).—These substances have been prepared in order to ascertain what influence the presence of a quinoline nucleus has on the colour of the already intensely coloured 1-aminoanthraquinone. The dinitration of 2-methylanthraquinone by concentrated nitric and sulphuric acids yields a mixture of 1:5-*dinitro-2-methylanthraquinone*, m. p. 251—252°, and 1:8-*dinitro-2-methylanthraquinone*, m. p. 189—190°, which is separated by the sparing solubility of the former in boiling glacial acetic acid. The two substances, the orientation of the nitro-groups in which is assumed from analogy to the course of the nitration of anthraquinone,

are reduced by alkaline sodium sulphide to 1 : 5-*diamino-2-methyl-anthraquinone*, m. p. 201—202°, red needles, and 1 : 8-*diamino-2-methylanthraquinone*, m. p. 206—208°, brownish-red needles, from which the quinolines are obtained by the Skraup method. 1-*Amino-2-methyl-anthraquinone-5-quinoline* (formula I), m. p. 206—207, reddish-brown



(I.)



(II.)

needles, dissolves in concentrated sulphuric acid with a brownish-yellow colour changing to blue by dilution with water. 1-*Amino-2-methylanthra-quinone-8-quinoline* (formula II), m. p. 100°, reddish-brown crystals, forms violet solutions in dilute mineral acids. C. S.

The Purification and Separation of Anthraquinoneacridones from By-products. Badische Anilin- & Soda-Fabrik (D.R.-P. 253090).—*Bromoanthraquinoneacridone*, a yellowish-red powder (prepared from anthraquinoneacridone), has m. p. above 300°, and is conveniently purified by isolation in the form of its *sulphate*, whilst the action of sulphuryl chloride on anthraquinoneacridone furnishes a mixture of two isomeric *chloroanthraquinoneacridones*. F. M. G. M.

[Preparation of 4 : 4′-Diamino-2 : 2′-dimethyldiphenylmethane.] Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 252916).—4 : 4′-*Diaminodiphenylmethane* prepared from *m*-toluidine crystallises from hot water in colourless needles, m. p. 123° ; the solution of its hydrochloride gives a violet coloration with ferric chloride, and when fully diazotised and combined with α-naphthol-5-sulphonic acid (2 mols.) furnishes a brownish-red azo-colouring matter. F. M. G. M.

Preparation of Aminobenzoyl Derivatives of Aminobenzoyl-7-amino-1-naphthol-3-sulphonic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 252159).—The tinctorial properties of the compounds obtained by the action of nitrobenzoyl haloids on aminobenzoyl-7-amino-1-naphthol-3-sulphonic acid and subsequent reduction have been recorded ; it is now found that these compounds can be obtained by the combination of an aminobenzoic acid with a nitrobenzoyl haloid, followed by condensation with 7-amino-1-naphthol-3-sulphonic acid and subsequent reduction. F. M. G. M.

Action of Hydroxylamine and of Phenylhydrazine on Urethanobenzylacetylacetone and on Ethyl Urethanobenzylacetoacetate. G. Bianchi (*Gazzetta*, 1912, **42**, ii, 496—512. Compare A., 1912, i, 542 ; Bianchi and Schiff, A., 1911, i, 977).—By the action of hydroxylamine on ethyl urethanobenzylacetoacetate, a stable

compound, $C_{16}H_{22}O_5N_2$, is obtained, which crystallises in colourless needles, m. p. 185° (sintering a few degrees previously). This compound is the normal *oxime*,

$$OH\cdot N:CMe\cdot CH(CO_2Et)\cdot CHPh\cdot NH\cdot CO_2Et.$$

The action of hydroxylamine on urethanobenzylacetylacetone yields two compounds. One, which forms heavy, prismatic crystals, m. p. 175° (decomp.), has the composition $C_{15}H_{20}O_4N_2$, and is the *monoxime*, $OH\cdot N:CMe\cdot CH(COMe)\cdot CHPh\cdot NH\cdot CO_2Et$; it is unstable and is obtained with difficulty. The other compound forms large, prismatic crystals, m. p. 94—95°; it is readily obtained and very stable; it has the composition $C_{15}H_{18}O_3N_2$ required by *4-urethano-benzyl-2 : 5-dimethyl*iso*oxazole*, $O<\begin{matrix}CMe:C\cdot CHPh\cdot NH\cdot CO_2Et \\ N=\!=CMe\end{matrix}$. The oxime readily changes into the *iso*oxazole derivative.

[With Manlio Rocchi.]—The action of phenylhydrazine on urethanobenzylacetylacetone and on ethyl urethanobenzylacetoacetate yields in each case the normal monophenylhydrazone. *Urethano-benzylacetylacetonephenylhydrazone*, $C_{21}H_{25}O_3N_3$, crystallises in groups of needles, m. p. 149—150° (decomp.). *Ethyl urethanobenzylaceto-acetatephenylhydrazone*, $C_{22}H_{27}O_4N_3$, crystallises in groups of needles, m. p. 136—137°. R. V. S.

Benzoylation of Aminourazole. Robert Stollé and K. Krauch (*Ber.*, 1912, 45, 3307—3311).—By the action of benzoyl chloride on aminourazole in presence of pyridine there are obtained a dibenzoylaminourazole, $C_2H_2O_2N_4(COPh)_2$, a tribenzoylaminourazole, and what was considered to be a tetrabenzoyl derivative. The last did not give aminourazole on hydrolysis, yielding instead a dibenzoyl derivative which proved to be identical with the benzoylhydrazi-carbonyl, $COPh\cdot N<\begin{matrix}NH \\ CO\end{matrix}$, obtained by Diels and Wagner (A., 1912, i, 511; compare Diels and Okada, *ibid.*, 918) by the action of alkali on chlorobenzoylcarbamide. The supposed tetrabenzoyl derivative is, therefore, *dibenzoylhydrazicarbonyl*, for which the symmetrical formula $CO<\begin{matrix}N\cdot COPh \\ N\cdot COPh\end{matrix}$ is considered most probable.

Dibenzoylaminourazole crystallises in needles, m. p. 201°, and yields aminourazole on hydrolysis.

Tribenzoylaminourazole forms tiny needles, m. p. 234°.

Dibenzoylhydrazicarbonyl has m. p. 130°. With sodium ethoxide, ethyl dibenzhydrazidoformate, m. p. 130° (Stollé and Benrath, A., 1904, i, 935), is obtained. On heating the carbonyl at 280°, 2 : 5-di-phenyl-1 : 3 : 4-oxadiazole is formed. E. F. A.

Constitution of the Compound from Benzoyl Chloro-carbamide and Alkali. Peter J. Schestakov (*Ber.*, 1912, 45, 3273—3274. Compare Diels and Okada, A., 1912, i, 918; Diels and Wagner, A., 1912, i, 511).—A claim for priority. Schestakov, Kind,

and Lebedev (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 330) have prepared the compound described as benzoyl hydrazicarbonyl,

$$COPh\cdot N<\begin{matrix}NH\\ |\\ CO\end{matrix},$$

by Diels and Okada, and ascribe to it the formula $COPh\cdot N<\begin{matrix}N\\ \|\\ C\cdot OH\end{matrix}$.

E. F. A.

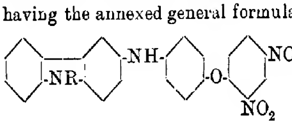
Preparation and Properties of 5-Aminoquinoline-6-carboxylic Acid and Certain Related Compounds. MARSTON T. BOGERT and HARRY LINN FISHER (*J. Amer. Chem. Soc.*, 1912, **34**, 1569—1576).—This investigation was undertaken with the object of preparing an aminocarboxylic acid of the anthranilic type from which substances belonging to new heterocyclic systems might be obtained.

A method is described for the preparation of 5-nitro-6-methylquinoline (Noelting and Trautmann, A., 1891, 325). 5-Amino-6-methylquinoline has m. p. 135° (corr.); attempts to oxidise this compound to 5-aminoquinoline-6-carboxylic acid were not successful.

5-*Aminoquinoline*-6-*carboxylic acid*, $NH_2\cdot C_9NH_5\cdot CO_2H$, m. p. 218·5° (decomp.), obtained in 30% yield by boiling 5-nitro-6-methylquinoline with alcoholic potassium hydroxide, crystallises in red nodules; it yields brown, amorphous precipitates with barium chloride, calcium chloride, cadmium iodide, copper sulphate, indium chloride, and mercuric chloride, and green precipitates with nickel chloride and silver nitrate. The *hydrochloride* has m. p. 264·7°. The *methyl* ester crystallises in bright red needles with $2H_2O$; the anhydrous form, m. p. 245° (corr.), is an amorphous, scarlet powder. 5-*Acetylamino*-6-*quinolinecarboxylic acid*, m. p. 237° (corr., decomp.), obtained by the action of acetic anhydride on the acid, forms slender, yellow needles; by prolonged heating with acetic anhydride it is converted into the *lactam*, $C_9H_5<\begin{matrix}CO\\ |\\ NAc\end{matrix}$ or $C_9H_5<\begin{matrix}CO\cdot O\\ |\\ N{=}CMe\end{matrix}$, m. p. 190° (uncorr.), which crystallises in nearly colourless needles, and reacts with primary amines to form naphtha*iso*triazines (this vol., i, 106). 5-*Benzylideneaminoquinoline*-6-*carboxylic acid*, $CHPh{:}N\cdot C_9NH_5\cdot CO_2H$, m. p. 221·4° (corr., decomp.), forms rosettes of needles. 5-*Hydroxyquinoline*-6-*carboxylic acid*, m. p. 211·7° (corr., decomp.), is obtained as a dark green precipitate by the action of nitrous acid on the hydrochloride of the amino-acid, and crystallises in rosettes of brown needles; it yields green, amorphous precipitates with barium chloride, zinc chloride, cadmium iodide, copper sulphate, mercuric chloride, and silver nitrate.

E. G.

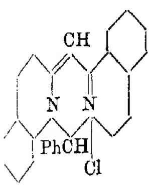
Preparation of Condensation Products from 1-Chloro-2:4-dinitrobenzene with the Leucoindophenols derived from Carbazole. LEOPOLD CASSELLA & Co. (D.R.-P. 252642).—Compounds having the annexed general formula, where R is hydrogen or alkyl, are obtained by the action of 1-chloro-2:4-dinitrobenzene on the leucoindophenols prepared from *p*-nitrosophenol with carbazoles. The *compounds* thus obtained



from the indophenols of carbazole with *p*-nitrosophenol (glistening, coppery leaflets, m. p. 190°) and from *N*-ethylcarbazole with *p*-nitrosophenol (small, reddish-brown needles, m. p. 223°) are described.

F. M. G. M.

Constitution of *iso*Quinoline Red. II. EDUARD VONGERICHTEN and W. HOMANN (*Ber.*, 1912, 45, 3446—3452. Compare A., 1910, i, 201).—The basic substance, $C_{19}H_{12}ON_2$, obtained together with benzaldehyde or benzoic acid by the oxidation of *iso*quinoline red by potassium dichromate and dilute sulphuric acid, proves to be *2-quinolyl-2-isoquinolyl ketone*, $C_9NH_6\cdot CO\cdot C_9NH_6$. It yields *iso*quinoline and quinaldic acid by heating with concentrated potassium hydroxide. It forms a *methiodide*, $C_{20}H_{15}ON_2I$, decomp. about 120°, and an *ethiodide*, decomp. about 160°. By treatment with aqueous silver sulphate, the methiodide yields a solution of the methosulphate, which is treated with sodium hydroxide and potassium ferricyanide, whereby quinaldic acid and *N*-methylisoquinolone are produced. By reduction with alcoholic ammonium sulphide at 200°, *iso*quinoline red yields benzyl mercaptan and a *substance*, m. p. 231°, golden-yellow leaflets.



The preceding statements, together with the fact that the quinaldine cannot be replaced by lepidine or any other methylated quinoline in the preparation of *iso*quinoline red, lead to the annexed formula for this substance.

C. S.

Octachloroindigotin and Some Derivatives of Tetrachloroanthranilic and Tetrachlorophthalic Acids. WILLIAM R. ORNDORFF and E. H. NICHOLS (*Amer. Chem. J.*, 1912, 48, 473—500).—By the action of dimethylaniline on the product of the diazotisation of tetrachloroanthranilic acid (Villiger and Blangey, A., 1909, i, 922), *dimethylaminobenzeneazotetrachlorobenzene-o-carboxylic acid*,

$$NMe_2\cdot C_6H_4\cdot N{:}N\cdot C_6Cl_4\cdot CO_2H,$$

is obtained as a brilliant red substance. The *acetyl* derivative of 5:6:7:8-tetrachloro-3:4-dihydro-2:4-benzoxaz-1-one (Villiger and Blangey, *loc. cit.*), m. p. 166·5° (corr.), crystallises in colourless, rectangular plates. When tetrachlorophenylglycine-*o*-carboxylic acid (A., 1910, i, 382) is boiled with acetic anhydride, *tetrachloroacetylindoxylic acid*, $C_6Cl_4{<}{}^{NAc-}_{C(OH)}{>}C\cdot CO_2H$, m. p. 225° (corr.), is produced as a pale yellowish-green, crystalline powder; its *silver* salt forms light greyish-green needles containing $1H_2O$. If fused sodium acetate is used with the acetic anhydride, the reaction proceeds further, and mono- and di-acetyl derivatives of tetrachloroindoxyl are produced; the *acetyl* derivative, $C_6Cl_4{<}{}^{NAc-}_{C(OH)}{>}CH$, m. p. 195° (uncorr.), crystallises in white, slender, microscopic prisms; the *diacetyl* derivative, $C_6Cl_4{<}{}^{-NAc-}_{C(OAc)}{>}CH$, m. p. 167° (uncorr.), forms very pale blue, rectangular prisms. On heating a solution of tetrachloroacetylindoxylic

acid in aqueous ammonia, *octachloroindigotin*,

$$C_6Cl_4<\genfrac{}{}{0pt}{}{NH}{CO}>C:C<\genfrac{}{}{0pt}{}{CO}{NH}>C_6Cl_4,$$

is produced as a purple, amorphous precipitate, which, when heated in a current of air at 360°, sublimes in small, rhombic plates.

Villiger's statement (A., 1909, i, 931) that dichlorophthalylhydroxylamine is converted into dichloroanthranilic acids by heating it with sodium carbonate solution, suggested that tetrachloroanthranilic acid might be similarly obtainable from the corresponding tetrachlorophthalylhydroxylamine (tetrachlorophthaloxime), and the following experiments were, therefore, carried out. When tetrachlorophthalic anhydride is heated with a solution of hydroxylamine in methyl alcohol, *tetrachlorophthaloxime hydroxide methyl ether*,

$$CO<\genfrac{}{}{0pt}{}{O}{C_6Cl_4}>C(OH)\cdot NH\cdot OMe,$$

m. p. 246—247° (corr., decomp.), is produced. If the tetrachlorophthalic anhydride is heated with an aqueous solution of hydroxylamine, *tetrachlorophthaloxime hydroxide*, $CO<\genfrac{}{}{0pt}{}{O}{C_6Cl_4}>C(OH)\cdot NH\cdot OH$, m. p. 254° (corr.), is obtained, which crystallises in nearly white prisms. When this substance is heated at 50° or left in a vacuum desiccator with phosphoric oxide, it loses water and becomes converted into *tetrachlorophthaloxime*, $C_6Cl_4<\genfrac{}{}{0pt}{}{CO}{C(:NOH)}>O$, which forms lemon-yellow prisms; the *sodium* salt is described; the *acetyl* derivative, m. p. 176° (corr.), crystallises in white needles. E. G.

[Preparation of Halogenated Derivatives of Indigoid Compounds.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252387).—The bisulphite compounds of indigoid derivatives are readily halogenated, yielding *compounds* with a high halogen content. The bromination of the bisulphite compounds obtained from isatin chloride and carbazole, and of that from indoxyl-red,

$$C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}>C:C<\genfrac{}{}{0pt}{}{CH}{C_6H_4}>N,$$

is described, and other compounds which can be similarly treated are mentioned. F. M. G. M.

Preparation of Condensation Products from Indigotin, its Homologues or Halogen-substitution Products. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250744).—When indigotin, its homologues, or halogen-substitution products are heated at 150—200° in the presence of zinc chloride with benzoic anhydride (or substituted benzoic anhydrides), condensation products are formed which find employment in the preparation of dyes.

Indigotin (10 parts), zinc chloride (10 parts), and benzoic anhydride (40 parts) at 150—160° yield a yellow, crystalline *compound*, m. p. 357°.

The following analogous *compounds* are also described: from dibromoindigotin with benzoic anhydride, yellow crystals, m. p. 340° (about) from indigotin with *p*-toluic anhydride, pale yellow crystals,

m. p. 330°; from the same with dibromoindigotin, m. p. above 330°: from indigotin with *p*-methoxybenzoic anhydride, yellow crystals, m. p. 320°; and from indigotin with *o*-chlorobenzoic anhydride, m. p. above 340°. These compounds dissolve in concentrated sulphuric acid with red colorations, but are insoluble in alkaline hyposulphite; they can be prepared in the presence of an indifferent solvent or by the fusion of the constituents. F. M. G. M.

Buchner's Pyrazolinecarboxylic Acids. CARL BÜLOW (*Ber.*, 1912, 45, 3349—3355).—A reply to Darapsky's criticism (A., 1912, i, 391) of the author's view that the additive products of ethyl diazoacetate with olefinic esters are really open-chain compounds (A., 1912, i, 134, 316). D. F. T.

Condensation Product of Formaldehyde, Ammonia, and Antipyrine. CARL MANNICH and W. KRÖSCHE (*Arch. Pharm.*, 1912, 250, 647—667).—Antipyrine condenses with formaldehyde and ammonia, or with the hexamethylenetetramine formed from these two substances, to give triantipyryltrimethyleneamine,

$$N(CH_2\cdot O\cdot C_{11}H_{11}N_2)_3,$$

in the formation of which antipyrine is believed to react in the enolic form represented by the formula $NPh<\begin{matrix}C(OH):C \\ | \\ NMe—CMe\end{matrix}$. A similar condensation occurs with antipyrine derivatives so long as these are not substituted in position 4.

Triantipyryltrimethyleneamine hydrochloride, $C_{36}H_{40}O_3N_7Cl,6H_2O$, m. p. 178°, or 206° (dry), formed when the condensation is effected by hydrochloric acid, is crystalline. The free *base*, m. p. 259—260°, crystallises anhydrous from methyl alcohol. When boiled with hydrochloric acid, it yields formaldehyde, ammonia, and methylenebisantipyrine, which yields a trihydrated dihydrochloride (Schuftan, A., 1895, i, 482), and a *monohydrochloride*, $CH_2(C_{11}H_{11}ON_2)_2,HCl,3H_2O$, m. p. 94—95°, which on drying at atmospheric temperature over sulphuric acid becomes *anhydrous*, then melts at 100—110°, and on solution in acetone deposits some *anhydrous dihydrochloride*, m. p. 200—220°, leaving some free base in solution.

On treatment with sodium hydrogen sulphite and sulphurous acid, triantipyryltrimethyleneamine yields antipyrine, which appears to be formed direct from the parent substance, since sulphurous acid has no action on methylenebisantipyrine.

Tritolypyryltrimethyleneamine, $C_{39}H_{45}O_3N_7,7H_2O$, m. p. 214—215° (dry), formed by condensing hexamethylenetetramine with tolypyrine (*p*-tolyl-2 : 3-dimethyl-5-pyrazolone), crystallises from a mixture of methyl alcohol and water; the *hydrochloride*, $C_{39}H_{46}O_3N_7Cl,6H_2O$, m. p. 100—105°, or 191° (dry), forms short, stout needles. Sulphurous acid in presence of sodium hydrogen sulphite hydrolyses it to tolypyrine, whilst hydrochloric acid converts it into ammonia, formaldehyde, and *methylenebistolypyrine*, m. p. 183—186°, or 190° (dry), which crystallises from 80% alcohol in slender needles, and can be prepared by condensing tolypyrine with formaldehyde.

Trihomoantipyryltrimethyleneamine, m. p. 280°, similarly obtained, crystallises from boiling methyl alcohol; the *hydrochloride*, m. p. 202°, crystallises from acetone. *Methylenebishomoantipyrine* crystallises from ethyl acetate in tablets with $1H_2O$, m. p. 120—130°, and after drying over sulphuric acid melts at 105—106°. The *dihydrochloride*,

$$C_{25}H_{30}O_2N_4Cl_2,3H_2O,$$

separates from 10% hydrochloric acid in stout crystals, m. p. 200—210°.

T. A. H.

Substituted α-Hydroxy- and α-Methyl-benziminazoles. OTTO KYM and L. RATNER (*Ber.*, 1912, 45, 3238—3255. Compare A., 1904, i, 453; 1911, i, 1044).—*p*-Nitro-*o*-phenylenediamine reacts readily with carbamide, forming 5-nitro-2-hydroxybenziminazole,

$$NO_2\cdot C_6H_3{<}{\substack{NH\\ N}}{\geqslant}C\cdot OH$$

(compare Hager, A., 1885, 149). This reacts with phosphoryl chloride forming 2-chlorobenziminazole, from which the 2-hydroxy-compound is regenerated on boiling with concentrated hydrochloric acid. Ammonia or aniline converts it into corresponding 2-amino- or 2-anilino-derivatives. The property of the azo-dyes of all phenylated benziminazoles to dye cotton persists, although to a less degree, in the 2-hydroxy-compounds.

Both 2-hydroxyl- and 2-methyl-benziminazoles can be nitrated without difficulty, forming dinitro-derivatives. It was found impossible to open the iminazole ring in these by Bamberger's method—by means of benzoyl chloride and sodium hydroxide.

Dinitro-2-hydroxybenziminazole when heated with aniline yields nitro-2-hydroxyanilinobenziminazole,

$$NHPh\cdot C_6H_2(NO_2){<}{\substack{NH\\ N}}{\geqslant}C\cdot OH,$$

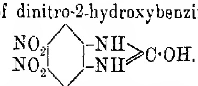
a red, crystalline compound, whereas the mononitro-2-hydroxybenziminazole does not react with aniline. This behaviour indicates that the second nitro-group has entered in the ortho-position to the first.

On reduction of the dinitro-compounds the diamino-compounds obtained behave as *o*-diamines, forming azimino-derivatives with nitrous acid and the corresponding dianhydro-derivatives when boiled with acetic acid. 2 : 7-Dimethylbenzdi-iminazole,

$$CMe{\leqslant}{\substack{NH\\ N}}{>}C_6H_2{<}{\substack{NH\\ N}}{\geqslant}CMe,$$

is shown to be identical with Nietzki's (A., 1887, 476, 477) diethenyl base obtained by nitration and reduction of diacetyl-*m*-phenylenediamine.

When 5 : 6-diamino-2-methylbenziminazole is fused with carbamide the dihydro-derivative already mentioned, 7-hydroxy-2-methylbenzdi-iminazole, $CMe{\leqslant}{\substack{NH\\ N}}{>}C_6H_2{<}{\substack{NH\\ N}}{\geqslant}C\cdot OH$, is formed. These changes confirm the structure of dinitro-2-hydroxybenziminazole as



5-Nitro-2-hydroxybenziminazole crystallises in yellowish-white needles,

m. p. 308°; it is strongly acid, dissolving in alkali hydroxide with an intense orange-yellow coloration. It further has weak basic properties.

5 : 6-*Dinitro-2-hydroxybenziminazole* separates in centimetre-long, lustrous needles, m. p. above 300°; the solution in cold dilute alkali hydroxide is intense red, and it forms a deep red, crystalline sodium salt.

5 : 6-*Dinitro-2-methylbenziminazole* forms yellowish-white needles, m. p. 223°.

Nitro-2-hydroxyanilinobenziminazole crystallises in red platelets, m. p. 298°.

Nitroamino-2-hydroxybenziminazole, prepared by heating the dinitro-compound with ammonia at 180—210°, forms bright red, lustrous crystals, m. p. above 300°; it is soluble in concentrated hydrochloric acid, and also dissolves in dilute sodium hydroxide or ammonia with a deep red coloration.

5 : 6-*Diamino-2-hydroxybenziminazole* readily oxidises as free base; the *hydrochloride* forms a brown, microcrystalline powder; the *diacetyl* derivative crystallises in lustrous, silky needles, m. p. 293—294°; 2-*hydroxybenzdi-iminazole*, $N{<}{\overset{NH}{\underset{N—}{}}}{>}C_6H_2{<}{\overset{NH}{\underset{—N}{}}}{>}C{\cdot}OH$, crystallises in yellow platelets, m. p. above 300°.

5 : 6-*Diamino-2-methylbenziminazole* crystallises in pale brown needles, m. p. above 300°; the *diacetyl* derivative separates in slightly pink-coloured, glistening needles, also m. p. above 300°. 2-*Methylbenzdi-iminazole* forms reddish-brown, stunted needles, m. p. above 300°.

2 : 7-Dimethylbenzdi-iminazole is obtained in lustrous, yellowish-white needles, m. p. outside the thermometer range.

7-*Hydroxy-2-methylbenzdi-iminazole* also forms lustrous, yellowish-white platelets, m. p. above 300°.

2-*Chloro-5-nitrobenziminazole* is a yellow, crystalline powder, m. p. 222—223°.

5-*Nitro-2-anilinobenziminazole* yields tiny, brown crystals, m. p. 278°.

5-*Nitro-2-aminobenziminazole* crystallises in a bulky mass of slender, yellow needles, m. p. 189—190°; the *acetyl* derivative is colourless.

E. F. A.

Constitution of Compounds from *o*-Diamines and α-Hydroxy-acids. Acetylation of Benziminazoles. AUGUSTIN BISTRZYCKI and GEORG PRZEWORSKI (*Ber.*, 1912, **45**, 3483—3495).—The product obtained by the interaction of 3 : 4-tolylenediamine and lactic acid is regarded as a tetrahydroquinoxaline by Georgescu, and as a benziminazole by Hinsberg. The authors now show that the latter view is correct and that the reaction is a general one; thus *o*-phenylenediamine and mandelic acid ($1\frac{1}{4}$ mol.) at 130—135° yield 2-α-hydroxybenzylbenziminazole; *o*-phenylenediamine and lactic acid (3 mols.) at 105—110° yield 2-α-hydroxyethylbenziminazole; 3 : 4-tolylenediamine and mandelic acid ($1\frac{1}{4}$ mol.) at 130—135° yield 2-α-hydroxybenzyl-5-methylbenziminazole, and 3 : 4-tolylenediamine and lactic acid yield 5-methyl-2-α-hydroxyethylbenziminazole. These substances are identical with Georgescu's so-called tetrahydroquinoxalones.

o-Phenylenediamine and glycollic acid at 120° yield 2-*hydroxymethyl*-

benziminazole, $C_6H_4<\substack{NH \\ N}>C\cdot CH_2\cdot OH$, m. p. 171—172°, colourless plates, which forms an *acetyl* derivative, m. p. 99—101°, by boiling with acetic anhydride and sodium acetate, and is oxidised by hot dilute alkaline potassium permanganate to *benziminazole-2-carboxylic acid*,

$$C_8H_6O_2N_2,2H_2O,$$

decomp. 169°, long prisms (*barium* salt, $C_{16}H_{10}O_4N_4Ba$), from which benziminazole is obtained by heating at 169°. The authors find that benziminazoles are readily acetylated by heating with acetic anhydride; thus benziminazole or benziminazole-2-carboxylic acid yields 1-*acetylbenziminazole*, m. p. 113—114°, long, prismatic needles, and 2-methylbenziminazole yields 1-*acetyl-2-methylbenziminazole*, m. p. 85—86°, colourless, microscopic needles or prisms.

3 : 4-Tolylenediamine and glycollic acid yield 5-*methyl-2-hydroxymethylbenziminazole*, m. p. 203°, plates or needles (*acetyl* derivative, m. p. 129—132°), from which Hinsberg's 5-methylbenziminazole-2-carboxylic acid, m. p. 156° (decomp.), is obtained by oxidation.

By oxidation with chromic and acetic acids, 2-α-hydroxybenzylbenziminazole yields 2-*benzoylbenziminazole*, $C_6H_4<\substack{NH \\ N}>C\cdot COPh$, m. p. 209—210° (decomp.), microscopic needles (*phenylhydrazone*, m. p. 185—186°, yellow plates; *phenylmethylhydrazone*, m. p. 225°, yellow prisms), and 2-α-hydroxybenzyl-5-methylbenziminazole yields 2-*benzoyl-5-methylbenziminazole*, m. p. 140—141°, felted needles.

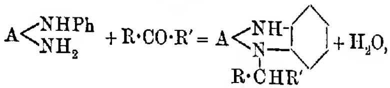
Equal molecular quantities of *o*-phenylenediamine and benzilic acid at 150—160°, or *o*-phenylenediamine (1·5 mol.) and chlorodiphenylacetic acid under the same conditions, yield a *substance*, $C_{20}H_{16}ON_2$, m. p. 221—223°, microscopic plates, which is probably 2-*hydroxydiphenylmethylbenziminazole*, $C_6H_4<\substack{NH \\ N}>C\cdot CPh_2\cdot OH$. The 5-methyl *homologue*, m. p. about 255°, is obtained from 3 : 4-tolylenediamine and chlorodiphenylacetic acid, whilst diphenylacetic acid and *o*-phenylenediamine yield 2-*benzhydrylbenziminazole*, $C_6H_4<\substack{NH \\ N}>C\cdot CHPh_2$, m. p. 218—220°, colourless, prismatic needles. C. S.

The Constitution of Acetyl-β-anthraquinonylmethylpyrazolone. RICHARD MÖHLAU (*Ber.*, 1912, 45, 3596).—The pyrazolone described recently (Möhlau, A., 1912, i, 704) is 4-acetyl-1-β-anthraquinonyl-3-methylpyrazolone. D. F. T.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. ALFRED SCHAARSCHMIDT (D.R.-P. 251480).—When *o*-diaminoanthraquinones are condensed with benzanthrone or anthraquinone, ω-di- or ω-tri-halogenmethyl derivatives, aldehydes, carboxylic acids, or their chlorides, they furnish iminazole condensation derivatives.

Compounds from the condensation of 1 : 2-diaminoanthraquinone with anthraquinone-2-carboxylic acid and with *benzanthronecarboxylic acid* (a yellow powder obtained from *p*-tolyl-*o*-benzoic acid, glycerol, and sulphuric acid), and from 2 : 3-diaminoanthraquinone with ω-dichloro-β-methylanthraquinone are described. F. M. G. M.

Preparation of Anthraquinone Derivatives containing Nitrogen. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252529).—The action of aldehydes on aryl-*o*-aminoanthraquinones has previously been described (A., 1907, i, 1085); when these are replaced by ketones the following action occurs:

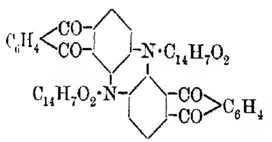


where A = anthraquinone, and R′ and R aryl or alkyl.

3-Bromo-2-amino-1-*p*-toluidinoanthraquinone (10 parts) when boiled with acetone (10 parts), zinc chloride (5 parts), and acetic acid (100 parts) yields a *compound*, bluish-red needles with metallic lustre; whilst *compounds* from the same base with acetophenone, and with isatin (blue needles), and from 3 : 7-dibromo-2 : 6-diamino-1 : 5-dianilinoanthraquinone with acetone are described in the original. These compounds all furnish soluble *sulphonic acids*, which dye wool in blue shades.

F. M. G. M.

[Preparation of Anthracene Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251021).—When the dyes obtained from di- and tri-anthrimides by the action of aluminium chloride are treated (in a paste) with sodium hypochlorite at 80° new compounds are formed.



Dianthraquinonylindanthren, $C_{56}H_{26}O_8N_2$ (annexed formula), orange-yellow needles, which decomposes at high temperatures with partial sublimation, is thus obtained from the product furnished by αα-dianthrimide; whilst the dye from 1 : 5-di-α : α-anthriminoanthraquinone and aluminium chloride yields under similar conditions a *compound* consisting of a reddish-brown powder.

F. M. G. M.

Indamines. FRITZ ULLMANN and JOHANN GNAEDINGER (*Ber.*, 1912, 45, 3437—3446).—Indamines are readily obtained by passing air through a cold dilute aqueous solution of equal molecular quantities of a meta-diamine and *p*-aminophenol hydrochloride after the addition of dilute sodium hydroxide (2 mols.); thus *m*-tolylenediamine and *p*-aminophenol yield 2-*amino*-4′-*hydroxy*-5-*methylindamine*,

$$NH{:}C_6H_2Me(NH_2){:}N{\cdot}C_6H_4{\cdot}OH,$$

decomp. about 165°, green metallic needles containing $3H_2O$. It is readily soluble in aqueous sodium hydroxide, and by reduction with alkaline sodium hyposulphite yields 2 : 4-*diamino*-4′-*hydroxy*-5-*methyldiphenylamine*, $C_6H_2Me(NH_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, m. p. 215°, colourless crystals (*sulphate*, $C_{13}H_{15}ON_3,H_2SO_4$, m. p. 202°). By the prolonged passing of air through its suspension in hot water, the indamine is converted into the *phenazine*, $NH_2{\cdot}C_6H_2Me{<}{\overset{N}{\underset{N}{|}}}{>}C_6H_3{\cdot}OH$, m. p.

above 360°, red needles with green reflex (*hydrochloride*, m. p. above 360°, red needles with green reflex; *diacetyl* derivative, m. p. 291°, darkening at 282°, yellow crystals).

m-Phenylenediamine and *p*-aminophenol yield Nietzki's so-called aminoindophenol, which, however, on account of its solubility in sodium hydroxide, is more suitably regarded as the hydroxyindamine, $NH:C_6H_3(NH_2):N\cdot C_6H_4\cdot OH$. The phenazine obtained by its further oxidation has m. p. above 360°, not 268° as given by Nietzki; also the diacetyl derivative has m. p. 275°, not 258°.

3'-Chloro-2-amino-4'-hydroxy-5-methylindamine,

$$NH:C_6H_2Me(NH_2):N\cdot C_6H_3Cl\cdot OH,$$

m. p. 185°, metallic violet needles containing H_2O, obtained from *m*-tolylenediamine and 2-chloro-*p*-aminophenol, yields *3'-chloro-2:4-diamino-4'-hydroxy-5-methyldiphenylamine*, m. p. 212°, colourless needles, by reduction, and the *phenazine*, $C_{13}H_{10}ON_3Cl$, m. p. above 360° (*diacetyl* derivative, m. p. 274°), by oxidation.

6-Chloro-*m*-phenylenediamine and *p*-aminophenol yield the *indamine*, $NH:C_6H_2Cl(NH_2):N\cdot C_6H_4\cdot OH$, decomp. 108°, metallic violet crystals containing H_2O (the corresponding *phenazine* and its *diacetyl* derivative have m. p. above 360° and 307° respectively), whilst 6-chloro-*m*-phenylenediamine and 2-chloro-*p*-aminophenol yield the *indamine*,

$$NH:C_6H_2Cl(NH_2):N\cdot C_6H_3Cl\cdot OH,$$

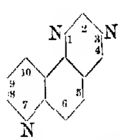
decomp. 128°, metallic violet needles containing H_2O.

By a similar process of oxidation, α-naphthol and *p*-aminophenol yield the *dihydroxyindonaphthol*, $OH\cdot C_6H_4\cdot N:C{<}{\scriptstyle\begin{matrix}C_6H_4\text{———}\\CH:C(OH)\end{matrix}}{>}CO$, m. p. 298°, glistening, green leaflets changing to a red powder at 120°. This substance, the constitution of which is proved by its formation from potassium β-naphthaquinone-4-sulphonate and *p*-aminophenol hydrochloride in cold aqueous solution, condenses with *o*-phenylenediamine in alcoholic solution to form the *hydroxyanilinonaphthazine*,

$$OH\cdot C_6H_4\cdot NH\cdot C_{10}H_5{<}{\scriptstyle\begin{matrix}N\\|\\N\end{matrix}}{>}C_6H_4,$$

m. p. 291°, orange crystals. C. S.

Synthesis of 1:3:7-Naphtha*iso*triazines: Derivatives of a New Heterocyclic System. MARSTON T. BOGERT and HARRY LINN FISHER (*J. Amer. Chem. Soc.*, 1912, **34**, 1576–1580).—In another paper (this vol., i, 98) the authors have described 5-aminoquinoline-6-carboxylic acid, its acetyl derivative, and the lactam of the latter. From these substances, compounds have been prepared containing the new nucleus (annexed formula), which is designated the 1:3:7-naphtha*iso*triazine nucleus.



*2:3-Dihydro-1:3:7-naphtha*iso*triazine-4-one* (*4-hydroxy-1:3:7-naphtha*iso*triazine*),

$$\begin{matrix}CH{=}N\\|\\NH\cdot CO\end{matrix}{>}C_9NH_5 \rightleftharpoons \begin{matrix}CH{=}N\\|\\N:C(OH)\end{matrix}{>}C_9NH_5,$$

m. p. 298·7° (corr.), obtained in 10% yield by heating 5-aminoquinoline-6-carboxylic acid with excess of formamide at 140° in

a sealed tube, crystallises in lustrous, pink prisms. The *2-methyl* derivative, m. p. above 300° (decomp.), prepared by boiling the lactam of 5-acetylaminoquinoline-6-carboxylic acid with solution of ammonia, forms slender, yellow needles, and, when heated with benzaldehyde and a few drops of acetic anhydride, yields the *2-styryl* derivative, $CHPh:CH\cdot C_{11}H_6ON_3$, m. p. above 300° (decomp.), as a yellow, crystalline powder. The 2 : 3-*dimethyl* derivative,

$$\begin{matrix}CMe{=}N\\ |\qquad\\ NMe\cdot CO\end{matrix}{>}C_9NH_5,$$

m. p. 178° (uncorr.), prepared by the action of methylamine on the lactam, crystallises in long, yellow needles. The *2-methyl-3-ethyl*, *2-methyl-3-n-propyl*, *3-phenyl-2-methyl*, and *3-p-anisyl-2-methyl* derivatives have m. p. 152·5° (uncorr.), 121—122° (uncorr.), 263—263·5° (corr.), and 246·9—247·9° (corr.) respectively. The *3-amino-2-methyl* derivative, m. p. 256·7° (corr.), obtained by the action of hydrazine on the lactam, is colourless; the *3-acetylamino-2-methyl* derivative has m. p. 268·5—269·5° (corr.), and the *3-benzylideneamino-2-methyl* derivative, m. p. 222·6° (corr.). The *3-anilino-2-methyl* derivative, $\begin{matrix}CMe{=}{=}{=}N\\ |\qquad\\ N(NHPh)\cdot CO\end{matrix}{>}C_9NH_5$, m. p. 249·5—250·5° (corr.), crystallises in pale brown needles.

1 : 2 : 3 : 4-*Tetrahydro*-1 : 3 : 7-*naphtha*iso*triazine*-2 : 4-*dione* (2 : 4-*dihydroxy*-1 : 3 : 7-*naphtha*iso*triazine*),

$$\begin{matrix}CO\cdot NH\\ |\qquad\\ NH\cdot CO\end{matrix}{>}C_9NH_5 \rightleftharpoons \begin{matrix}C(OH):N\\ |\qquad\\ N:C(OH)\end{matrix}{>}C_9NH_5,$$

m. p. above 300°, is obtained as a yellow or brown powder by fusing a mixture of 5-aminoquinoline-6-carboxylic acid and carbamide.

E. G.

[Preparation of Anthracene Derivatives.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 253088).—It is found that the previously described ψ-azimino-compounds (A., 1912, i, 1035) obtained by oxidising the azo-compound formed by coupling 2-aminoanthracene with diazotised 2-aminoanthraquinone can be nitrated, and the so-obtained *nitro-* or *dinitro*-compounds reduced with sodium sulphide or alkaline sodium hyposulphite to the corresponding *amino-* or *diamino*-compounds. The nitrated products are greenish-yellow, and the amino-derivatives, brownish-black, powders.

F. M. G. M.

Methyliminothiotriazine. ADRIANO OSTROGOVICH (*Chem. Zentr.*, 1912, ii, 607; from *Bull. Soc. Şti. Bucureşti*, 1912, 21, 27—31).—The 2-imino-6-thiol-4-methyl-1 : 3 : 5-triazine, already described (A., 1912, i, 320), on oxidation with nitric acid (D 1·4) yields cyanuric acid, and with alkaline permanganate gives iminoketomethyltriazine (A., 1904, i, 832), the picrate of which melts at 221—221·5°, not 121—121·5° as stated previously. Iminothiolmethyltriazine does not give up its sulphur to mercuric oxide, but yields a stable mercury salt when mercuric chloride is added to its solutions in aqueous sodium hydroxide.

T. A. H.

Quadriurates. WILLEM E. RINGER and J. I. J. M. SCHMUTZER (*Zeitsch. physiol. Chem.*, 1912, **82**, 209—220. Compare Kohler, A., 1911, i, 243, 690).—The hypothesis that the so-called quadriurates are mixed crystals has been tested experimentally, a series of quadriurates of varying composition having been examined chemically and crystallographically. This hypothesis is satisfactory when it is assumed that the urates represent solid solutions of uric acid in ordinary mono-metal urates, which are formed at high temperatures, but are unstable at lower temperatures, and tend to part with the excess of uric acid.

E. F. A.

Preparation of Aminobenzoylamino-compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252376).—When sodium diaminobenzoyldiaminostilbenedisulphonate is fused during half an hour with *p*-nitrobenzoyl chloride and the *di*-p-*nitrobenzoyl* derivative subsequently reduced with iron and acetic acid, it furnishes the *compound*, $C_2H_2[C_6H_3(SO_3Na)\cdot NH\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2]_2$.

Other analogous compounds with valuable tinctorial properties can be obtained in the benzidine, tolidine, or dianisidine series.

F. M. G. M.

Separation of Proteoses by Ultra-filtration. EDGARD ZUNZ (*Bull. Acad. roy Belg.*, 1912, 656—674. Compare A., 1911, i, 1050). —The composition of the filtrate obtained from identical solutions of Witte's peptone, submitted under the same conditions to Bechhold's method of ultra-filtration, varies appreciably from filter to filter, although the latter are made as alike as possible. Further, the filtrate varies during the course of the same experiment, at one time the ultra-filter allowing certain proteoses to pass and at another time retaining a portion of them. The four groups of proteoses established by Pick cannot be satisfactorily separated by successively employing ultra-filters with smaller and smaller pores. The ultra-filtration causes a dissociation of each of these groups of proteoses into several fractions. In these groups the proteoses, the aliphatic amino-nitrogen of which can be detected by van Slyke's method, pass completely through an ultra-filter made by means of a 6% collodion solution.

W. G.

Changes in the Physical Conditions of Colloids. XIV. The Hydration of Various Protein Compounds, with Special Reference to the Action of Caffeine. WOLFGANG PAULI and OSKAR FALEK (*Biochem. Zeitsch.*, 1912, **47**, 270—299).—The general theory of Pauli's as to the high degree of hydration of the protein ion is confirmed by a series of measurements of the changes of viscosity of well dialysed gelatin solutions on addition of acids and alkalis, in both of which cases well-marked maxima are observed. According to the theory, salts combine with the protein, and when these are present, the number of free proteins ions is diminished. The addition of salts diminishes the viscosity, and this effect was quantitatively measured in the case of several salts.

Caffeine has, however, a peculiar action on the ox- and horse-serum proteins, in that it increases the viscosity of the acid-protein mixtures

(and according to Pauli the state of hydration in solution). This effect has been measured in a large number of cases. The magnitude of the effect is also influenced by the nature of the acid employed. A similar effect was produced by theophylline, but not by diethylglycinamine caffeine or caffeine ethylenediamine, both of which produce a depression of viscosity. Caffeine does not effect the hydration of gelatin or fibrin, as it does not cause these substances to take up more water. The reason of the peculiar action of caffeine on certain proteins may be due to formation of complex double compounds. It does not appear to be due to direct salt formation, as determined by the effect of addition of caffeine to protein solutions on the electrolytic conductivities, the osmotic pressures, or the hydrogen-ion concentrations as measured by the electrometric method. S. B. S.

The Oxidation Relations of Certain Heavy Metals in Combination with Protein, and Some Physico-chemical Properties of the Same. II. Carlo Cervello and Corrado Varvaro (*Arch. expt. Path. Pharm.*, 1912, **70**, 369—374).—The coagulation rate of zinc albuminate and mercury albuminate is greater than that of the simple protein, but less than that of the albuminates of manganese and copper. Iron albuminate is not altered by boiling. Complete coagulation with precipitation of denaturated protein is only obtained with zinc albuminate. In weakly acid or neutral solutions, the other metallic albuminates give only a cloudy fluid on heating: this is most marked with mercury, and least with manganese albuminate. In reference to their oxidative powers, as measured by the effect on indigotin and similar substances, the albuminates of iron and copper are most energetic; those of mercury, zinc, and manganese follow in the order named. The albuminates therefore behave like simple metallic salts. W. D. H.

The Kyrine Fraction obtained on Partial Hydrolysis of Proteins. I. Phœbus A. Levene and F. J. Birchard (*J. Biol. Chem.*, 1912, **13**, 277—289).—Siegfried's hypothesis regarding kyrine is that it is a fragment of the protein molecule which resembles natural protamines. The kyrine fraction obtained in the present research by Siegfried's method of partial hydrolysis of gelatin yielded on hydrolysis arginine, lysine, glutamic acid, glycine, and proline in peptide linking. Probably two peptides were present, one containing lysine and three monoamino-acids, and the other, arginine and one monoamino-acid. Further investigations are being prosecuted. W. D. H.

The Isoelectric Point of Casein. Leonor Michaelis and H. Pechstein (*Biochem. Zeitsch.*, 1912, **47**, 260—268).—The isoelectric point was determined by ascertaining the optimal mixture for precipitation of sodium acetate and acetic acid solutions, and also by the method of electrocataphoresis. In the former case the salt concentrations in the various series of experiments were kept constant, and in the latter case, the salt content was kept very low. By these methods the isoelectric point was found to be $2{\cdot}5 \times 10^{-5}$ and $2{\cdot}4 \times 10^{-5}$.

respectively. In the presence of salts a certain asymmetry of behaviour was observed, in that after twenty-four hours excess of acid above the isoelectric point allowed greater precipitation than deficit of acid.

S. B. S.

Blood Pigment. LÉON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 82, 413—414. Compare Grabowski and Marchlewski, A., 1912, i, 1015).—The conclusion that hæmopyrrole whether derived from blood pigment or chlorophyll contains 3-methyl-4-ethylpyrrole is confirmed by Piloty and Stock (A., 1912, i, 923), who obtain the same substance from hæmin. The synthesis of chlorophyll in plants begins probably with that of 3-methyl-4-ethylpyrrole.

E. F. A.

Nomenclature of Derivatives of the Blood Pigment. KARL BÜRKER (*Zeitsch. physiol. Chem.*, 1912, 82, 346).—Instead of Abderhalden's (A., 1912, i, 521) nomenclature of hæmatin for hæmochromogen and oxyhæmatin for hæmatin, it is suggested to use the terms reduced hæmatin and oxyhæmatin.

E. F. A.

Methylation of Hæmin. IV. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1912, 82, 113—159).—In the preparation of hæmin by Mörner's method using methyl alcohol, a crude product is obtained in satisfactory amount containing very little protein, which usually consists mostly of methylhæmin mixed with a little dimethylhæmin. There is evidence that there are two methylhæmins, one or the other being formed from ox-blood according to the conditions. One isomeride is insoluble in 5% sodium carbonate; the other is soluble in sodium carbonate, and also in 0·7% potassium carbonate. The dissolved dye contains chlorine.

The first isomeride loses chlorine without dissolving, and forms a methylhæmatin; a similar compound is formed by the action of methyl-alcoholic sodium hydroxide.

The dehydrochloride products prepared from the methylhæmins are of different composition, the one being normal, the other having taken up a molecule of water.

Methylhæmatin and hæmatin when dissolved in methyl alcohol containing sulphuric acid and the boiling solution precipitated by hydrochloric acid yield dimethylated products which do not contain the calculated proportion of chlorine for hæmin derivatives and are soluble in acidified methyl alcohol. Dehydrochloromethylhæmin under similar treatment does not show a complete addition of hydrogen chloride.

Dehydrochlorohæmin is converted into dimethylhæmin. Dimethylhæmin forms a dimethylated dehydrochloro-product.

Methylhæmin is hydrolysed by more than three molecules of 1% sodium hydroxide in the cold; dimethylhæmin requires warming to effect hydrolysis. Dimethylhæmin is readily converted into dimethylhæmatin by the action of methyl alcoholic sodium hydroxide.

E. F. A.

Preparation of Hæmatoporphyrin from Carbon Monoxide Blood. VINZENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1912, 82, 273—275).—Pure hæmatoporphyrin, particularly suited for spectroscopic work and free from brown-coloured impurities, is obtained by completely replacing the oxygen in blood by carbon monoxide before acting on it with sulphuric acid. E. F. A.

Formation of Porphyrin. HANS FISCHER and FRIEDRICH MEYER-BETZ (*Zeitsch. physiol. Chem.*, 1912, 82, 96—108).—The exact conditions for the preparation of mesoporphyrin are described. On oxidation with lead peroxide in acid solution, methylethylmaleinimide,

$$NH\!<\!\begin{matrix}CO\cdot CEt\\ \|\\ CO\cdot CMe\end{matrix},$$

and hæmatic acid, $NH\!<\!\begin{matrix}CO\cdot CMe\\ \|\\ CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}$, are obtained. On reduction by means of hydrogen iodide in acetic acid and phosphonium iodide, the same products were obtained as are given by hæmin, including hæmopyrrole and phonopyrrolecarboxylic acid. Mesoporphyrin is considered to be a simple reduction product of hæmin minus its iron. Possibly the porphyrin spectrum is due to the elimination of the complex iron grouping from hæmin; in fact, the complex iron salt of porphyrin shows the hæmin spectrum. It is probable that two alcoholic hydroxyl groups are reduced in the formation of mesoporphyrin.

Pure mesoporphyrin has no poisonous photobiological action, whereas hæmatoporphyrin when injected subcutaneously into mice which are exposed to light causes death. E. F. A.

[Guanylic Acid.] IVAR BANG (*Biochem. Zeitsch.*, 1912, 46, 500—501).—The author believes that the guanylic acid recently isolated in the form of a crystalline brucine salt by Levene and Jacobs (A., 1912, i, 926) is not guanylic acid itself, but a scission product. S. B. S.

The Pentose of Guanylic Acid. KG. O. AF KLERCKER (*Biochem. Zeitsch.*, 1912, 47, 331—342).—The author gives a general view of the literature concerning the sugar derived from the pancreatic nucleic acid, guanylic acid, and allied substances. He prepared the osazone from guanylic acid, and obtained rotations of $-0\cdot59$ to $-0\cdot64°$ for 0·2 gram in 10 c.c. for various preparations recrystallised from alcohol. For *l*-arabinose preparations obtained in the same way he obtained numbers from $+0\cdot62$ to $0\cdot69°$, and for *l*-xylose preparations $-0\cdot67$ and $0\cdot70°$. The sugar from which the guanylic acid pentosazone was prepared was lævorotatory, and as xyloses yield osazones which rotate in the opposite direction to the sugars themselves, the conclusion is drawn that the guanylic acid pentose is not *l*-xylose, but probably belongs to the *d*-arabinose group. The conclusion is also supported by the general character of the osazones as regards behaviour on crystallisation and appearance. Nevertheless, the author states that the optical properties of the phenylpentosazones do not

form a satisfactory *criterion for distinguishing between the various sugars.* S. B. S.

The Optimal Hydrogen-ion Concentration for the Liquefaction of Gelatin by Trypsin. Sven Palitzsch and L. E. Walbum (*Biochem. Zeitsch.*, 1912, **47**, 1—35).—Fermi's method was employed, but was modified in two particulars, in that, firstly, boracic acid was added to the gelatin to avoid change of hydrogen-ion concentration during the digestion, and, secondly, the digestion mixture was neutralised after completion of the action of trypsin, so that the actual cooling process took place at the same hydrogen-ion concentration, for it was found that solutions of undigested gelatin solidified more slowly in alkaline than in neutral solutions in the absence of boric acid, although there was not much difference when this acid was present. By means of this method it was found that the optimal conditions for liquefaction were at the following hydrogen-ion concentrations: at 30°, $10^{-9 \cdot 9}$; at 37°, $10^{-9 \cdot 7}$; at 45°, $10^{-9 \cdot 3}$; at 55°, $10^{-8 \cdot 0}$; that is to say, the higher the temperature, the nearer to the neutral point is the hydrogen-ion concentration for tryptic activity when measured by the Fermi process. S. B. S.

The Mechanism of Pepsin Digestion. Johanne Christiansen (*Biochem. Zeitsch.*, 1912, **47**, 226—249).—The viscometric method was adopted, and in the preliminary experiments on the action of acid on genuine proteins (dialysed serum proteins, etc.), it was found that the addition of acid increased the viscosity of the solutions up to a certain maximum point, after which further additions caused a diminution. The Günzburg reaction for hydrochloric acid becomes positive at the point of maximal viscosity, thus bearing out Pauli's theory that at this point the solution contains essentially chlorine ions and heavily hydrated protein ions. The viscosity is diminished by filtration through paper, more especially when only just sufficient acid is present to produce the maximum readings. With larger excess of acid, the effect of filtration becomes less marked. Similar results were obtained on filtration of mixtures of protein and alkali, and the results indicate that the protein ion is adsorbed by the paper. In investigating the action of pepsin, viscosity changes of mixtures having the same initial viscosity but different amounts of acid (that is, amounts of acid less and more than necessary to produce a mixture with the maximum viscosity) were chosen. It was found that such corresponding mixtures, under the influence of pepsin, changed their viscosities at the same rate, which fact seems to indicate that in the neighbourhood of maximal viscosity the rate of pepsin action is independent of the hydrogen-ion concentration. This result is not in accordance with results obtained with coagulated egg-white, which requires a certain excess of acid for maximal digestion rate. The difference is ascribed to the change in the character of the protein. Preliminary experiments carried out with dialysed sheep serum-albumin, in which the rate of formation of acid albumin was ascertained (this is only formed in this case when pepsin is present as well as acid), also indicated that the maximum rate of formation of this product takes place at the

point of maximum viscosity (that is, when there are the maximum number of protein ions present). S. B. S.

The Enzymes of the Pancreas. I. The Generation of Trypsin from Trypsinogen by Enterokinase. JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1912, **45**, 370—388).—The time occupied in activating trypsinogen by enterokinase is a function of the amount of the latter enzyme added. As the action proceeds, trypsin is produced at a constantly increasing rate. The reaction is accelerated by rise of temperature; it occurs best in a neutral medium, is delayed by alkali, and stopped by acid. There is no evidence that trypsin can activate trypsinogen, or that trypsin acts as a co-enzyme to enterokinase. Proteins apparently delay activation, because the trypsin first formed is adsorbed by the protein; the delay varies in different proteins. The following theory is advanced: Enterokinase is a proteolytic enzyme acting best in a neutral medium; trypsinogen contains a protein moiety with which trypsin is combined, and in this combination the proteolytic properties of trypsin are masked. The generation of trypsin from trypsinogen by enterokinase depends on the adsorption of the enterokinase by the protein moiety of the trypsinogen; digestion of the protein moiety follows, and trypsin is thus liberated. W. D. H.

Action of Hydrogen Chloride on Invertase. II. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, **82**, 377—390. Compare following abstract).—Purified invertase takes up considerable quantities of hydrogen chloride, losing its specific activity. The greater part of the hydrogen chloride is removed on keeping in a vacuum, but the hydrolytic activity is not regained.

The invertase preparation contained 5·57% of nitrogen, 2·3% being amide nitrogen and 3·17% titratable in presence of formaldehyde. The ash amounted to 22·2%; the acidity was five to six times as large as in the case of purified diastase.

The destruction of the enzymic activity is not due to the formation of salts with the basic or other atomic groups of the enzyme, but the action of the acid reduces the amount of nitrogen which can be titrated in presence of formaldehyde, pointing to the formation of condensation products between the carboxyl and amino-groups.

The active component of invertase accordingly possesses a different constitution from that of diastase. E. F. A.

Action of Hydrogen Chloride on Diastase. I. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, **82**, 276—325).—When dry hydrogen chloride is passed over purified diastase the enzyme takes up a good deal of the gas, forming with it a loose chemical compound; the enzyme loses its specific activity. On exposure in a vacuum the hydrogen chloride is removed and the activity of the enzyme restored. It is shown that the hydrogen chloride is not fixed to the amide or secondary nitrogen atoms of the enzyme complex, and that only part is attached to the basic groups. The action of the acid does not cause any particular hydrolysis of the enzyme molecule. The specific

enzyme action of diastase is due to the atomic groups which can fix hydrogen chloride. E. F. A.

Malt Diastase, and the Action of Potassium Phosphates on It. RUTGER C:SON HEYL (*J. pr. Chem.*, 1912, [ii], 86, 433—457). —The author has studied the diastatic hydrolysis of starch under various conditions by determining the amount of maltose produced, according to Bertrand's method (A., 1907, ii, 136).

In the first part of its course, the diastatic actions follow the logarithmic curve, and in such a manner as if only a part of the starch were capable of hydrolysis.

The magnitude of this part depends on the concentration of the starch and of the enzyme, and also on the presence of electrolytes and proteins. In the last part of its course, the reaction proceeds with extreme slowness.

Potassium dihydrogen phosphate exercises an activating influence on the enzyme, and the same is true with respect to the action of dipotassium hydrogen phosphate on old solutions of the enzyme; in freshly prepared solutions the latter salt exerts a retarding influence.

The activating action of the phosphates is considerably influenced by the presence of proteins in the enzyme solutions. F. B.

Reaction between Enzymes and Other Substances. SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1912, 82, 175—178).—Introductory to following paper. W. D. H.

The Action of Certain Colloids on the Inhibition of Enzyme-actions. G. JAHNSON-BLOHM (*Zeitsch. physiol. Chem.*, 1912, 82, 178—208).—Saponin completely hinders the inhibitory effect of charcoal on rennet, and partly that of normal serum. The saponin appears to liberate the enzyme which is adsorbed by the charcoal, and the reaction is a rapid one. It is accelerated by elevation of temperature, and by increase in the amount of saponin. Saponin increases the inhibitory effect of immune serum on rennet. Saponin partly activates a solution of rennet-zymogen. It acts similarly on trypsin adsorbed by charcoal, but has no effect on the antitryptic action of serum-albumin. Cholesterol acts like saponin on charcoal and rennet, but increases the inhibitory effect of normal serum. It has no influence on the antitryptic action of charcoal and serum-albumin. Egg-white if treated with hydrochloric acid and neutralised, partly inhibits the anti-rennetic power of normal serum. W. D. H.

The Coagulation of Milk by Rennet. JOHN MELLANBY (*J. Physiol.*, 1912, 45, 345—362).—The clotting of milk by pancreatic rennet follows the same general laws as that by gastric rennet, but the two enzymes are distinct, because they differ in the effect of alkali on them; their anti-enzymes in serum are specific, and pancreatic rennet requires a greater amount of calcium than gastric rennet does. In the case of both enzymes, calcium salts may be replaced by salts of barium, strontium, or magnesium. There is no indication from electrical conductivity determinations that calcium enters into chemical com-

ination during the curdling process. The hypothesis is advanced hat all proteolytic enzymes curdle milk, provided suitable conditions re provided; those, like pepsin, which act best in an acid medium equiring less calcium than those which, like trypsin, act in a alkaline medium. The coagulation of milk is due to the adsorption of the nzyme by the caseinogen, and the enzyme-caseinogen complex is recipitated by the bivalent calcium ions of the milk; the quantity of nised calcium salt required to effect precipitation is intimately elated to the quantity of enzyme adsorbed. A method based on this ypothesis is described for the detection and estimation of proteolytic nzymes. W. D. H.

The Biochemical Rôle of Peroxydases in the Transformaion of Orcinol into Orcein. JULES WOLFF (*Compt. rend.*, 1912, 55, 1031—1032. Compare A., 1912, i, 928).—The action of ammonia nd atmospheric oxygen on orcinol in dilute solutions is a very slow xidation, this being the first condition for the formation of orcein. he introduction of a peroxydase influences far more the formation f the colouring matter than the amount of oxygen absorbed.

W. G.

The Nomenclature of the Polyphenoloxydases. FR. BATELLI nd (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, 46, 395—396).—The uthors recommend the term *polyphenoloxydase* to indicate an enzyme hich accelerates the oxidation of polyphenols and the corresponding mino-derivatives. Such ferments are to be distinguished from those the character of tyrosinase, which acts similarly on monophenols, nd which are designated simply *phenoloxydases*. The expression enolase is to be avoided in this sense, as it indicates a ferment which celerates the hydrolysis of an aromatic ester. S. B. S.

Preparation of Organic Arsenic Compounds. HEINRICH BART D.R.-P. 250264. Compare La Costa and Michaelis, A., 1880, 36; Schraube and Schmitt, A., 1894, i, 237).—The following ganic arsenic compounds have been obtained by treating diazotised lutions of the following bases with sodium arsenite and subsequently ating in the presence of sodium hydroxide until the evolution of itrogen ceases. p-*Bromophenylarsinic acid* (colourless needles) from bromoaniline; o-*benzoarsinic acid* (colourless needles) from *o*-aminonzoic acid; p-*acetylaminophenylarsinic acid* from monoacetyl-*p*-enylenediamine; *p*-tolylarsinic acid (Abstr., 1880, 396) from toluidine: and *compounds* from potassium *iso*diazobenzene and nitro*iso*diazobenzene; from 4-nitro-2-aminophenol; from *p*-nitroiline (which is best decomposed in tartaric or oxalic acid solutions), d from the same base decomposed in the presence of sodium *p*-nitroenylarsenite; whilst *p*-aminophenylarsinic acid furnishes *benzeneliarsinic acid.*

The *sodium* salts of these compounds are colourless or grey needles, d the original contains numerous formulæ illustrating possible ases in their formation. F. M. G. M.

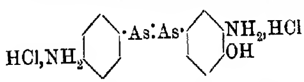
Preparation of Derivatives of 3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250745).—When 3 : 3′-diamino-4 : 4′-hydroxyarsenobenzene is treated with halogenated acetic acid (or its homologues) in aqueous alkaline solution it yields neutral, soluble compounds of therapeutic value.

The *compound*, $NH_2 \cdot C_6H_3(OH) \cdot As{:}As \cdot C_6H_3(OH) \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained when 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (100 parts), dissolved in a mixture of methyl alcohol (300 parts), and water (300 parts) containing sodium hydroxide (4 mols.), is treated with chloroacetic acid (50 parts) and potassium iodide (36 parts) and heated at 60—65° during two to three hours in an indifferent gas with exclusion of air; the product is isolated by the limited addition of acid. The brownish-yellow *sodium* salt is precipitable with alcohol; the *potassium* and *ammonium* salts forms similar powders.

The *compound*, $NH_2 \cdot C_6H_3(OH) \cdot As{:}As \cdot C_6H_3(OH) \cdot NH \cdot CHMe \cdot CO_2H$, a yellow powder, is prepared in a similar manner with α-bromopropionic acid, and furnishes *alkali* salts, whilst *diaminodihydroxyarsenobenzenediacetic acid*, $As_2[C_6H_4(OH) \cdot NH \cdot CH_2 \cdot CO_2H]_2$, is obtained with bromoacetic acid. F. M. G. M.

Preparation of Unsymmetrical Aromatic Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251104).—When an equimolecular mixture of two arylarsinic acids (or oxides) is reduced it yields an unsymmetrical aromatic arseno-compound.

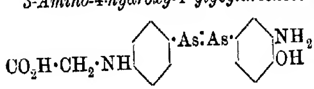
3 : 4′-*Diamino-4-hydroxyarsenobenzene hydrochloride* (annexed formula), a yellow, microcrystalline powder, is obtained as follows:



p-Aminophenylarsinic acid (21·7 parts) or its equivalent of *p*-aminophenylarsenious oxide (A., 1909, i, 347) and 23·3 parts of 3-amino-4-hydroxyphenyl-1-arsinic acid (A., 1910, i, 803) in methyl alcohol (100 parts) and concentrated hydrochloric acid (39 parts) is slowly stirred into a mixture of stannous chloride (100 parts) dissolved in alcohol (300 parts) to which has been added 500 parts of alcohol saturated with hydrogen chloride and 17 parts of hydriodic acid (D 1·7), the temperature meanwhile being maintained at −5° to −10°; the product is slowly precipitated in crystalline form. The *sulphate* forms a flocculent, yellow insoluble precipitate.

Phenylglycylarsenious chloride, $AsCl_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H,HCl$, a crystalline paste which can be washed with acetic acid and ether, is prepared by reducing a concentrated hydrochloric acid solution of phenylglycylarsinic acid (to which a trace of hydriodic acid has been added) with sulphurous acid at −10°; it is decomposed readily by alkalis to the corresponding hydroxide.

3-*Amino-4-hydroxy-4′-glycylarsenobenzene* (annexed formula) is obtained as a viscous, yellow paste when molecular proportions of the foregoing chloride and 3-amino-4-hydroxyphenyl-



arsenious oxide (A., 1911, i, 1055) in methyl-alcoholic solution are reduced with sodium hyposulphite at the ordinary temperature.

3′:5′-*Dichloro-3-amino-4:4′-dihydroxyarsenobenzene*, a yellow powder, is prepared from 3-amino-4-hydroxyarsenious oxide and 3:5-*dichloro-4-hydroxyphenylarsenious oxide*, $AsO\cdot C_6H_2Cl_2\cdot OH$, which latter compound is obtained by the reduction of dichloro-*p*-hydroxyphenylarsinic acid (*loc. cit.*); 3-*amino-4-hydroxyarsenobenzene*, $C_6H_5\cdot As_2\cdot C_6H_3(NH_2)\cdot OH$, a fawn-yellow powder, is prepared from phenylarsenious oxide and 3-amino-4-hydroxyphenylarsenious oxide. F. M. G. M.

Preparation of Products Reduced Beyond the Arseno-stage from Substituted Aromatic Arsinic Acids. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 251571).—It is found that when powerful reducing agents (such as tin, zinc, or iron) in concentrated acid solution act on arylarsinic acids that they can be reduced beyond the arseno-condition (compare Palmer and Dehn, A., 1902, i, 86).

The following *compounds* are described:

(1) From *p*-hydroxyphenylarsinic acid as a colourless precipitate, soluble in alkalis, and isolated by means of carbon dioxide; it darkens at 75° and decomposes violently at 155°.

(2) From *p*-aminophenylarsinic acid, a colourless oil, b. p. 132°/10 mm., which exposed to air is rapidly converted into diaminoarsenobenzene.

(3) From phenylglycylarsinic acid, a colourless precipitate which rapidly darkens, and is isolated in the form of its *zinc* salt.

(4) From 3-nitro-4-hydroxyphenylarsinic acid (A., 1910, i, 803), isolated as its *zinc* salt; the free *arsine* is a colourless powder darkening at 100° and decomposing violently at 135°.

F. M. G. M.

Formation of Organo-metallic Compounds during Electrolytic Reductions. Julius Tafel (*Ber.*, 1912, 45, 3321).—Polemical against Law (T., 1912, 101, 1016, 1544). A claim for priority. Law's statement that the formation of organo-metallic compounds at mercury cathodes has never been observed is incorrect (compare A., 1906, i, 941; 1911, i, 764). T. S. P.

Chemico-therapeutical Researches on Mercury Compounds. Mercuridi-*p*-aminophenol. Ernest Fourneau and A. Vila (*J. Pharm. Chim.*, 1912, [vii], 6, 433—441).—p-*Nitrophenylmercuric acetate*, $C_8H_7O_5NHg$, obtained by the action of mercuric acetate on sodium *p*-nitrophenol dissolved in boiling water, crystallises in flattened, colourless needles, and on treatment with carbon dioxide furnishes the corresponding *oxide* (compare A., 1911, i, 1056). The latter by a complex series of reactions, which are discussed in detail in the original, gives with sodium sulphide, *sodium di*-p-*nitromercuridiphenol*, $C_{12}H_{10}O_6N_2HgNa_2$, crystallising in garnet-red needles, from which the corresponding *mercuridi*-p-*nitrophenol* is liberated by the action of acids. This on reduction in alkaline solution by sodium hyposulphite yields *di*-p-*aminomercuridiphenol*, $Hg[C_6H_3(OH)NH_2]_2$, crystallising in heavy needles, insoluble in water, but readily soluble in alcohol; the *hydrochloride* forms brilliant needles soluble in water. The free base oxidises rapidly in alkaline solution on exposure to air.

This substance is toxic, producing the ordinary symptoms of mercurial poisoning, due no doubt to the liberation of simple mercury derivatives by oxidation in the organism. The *acetyl* derivative crystallises in slender needles, is soluble in alkalis, forming stable solutions, and is much less toxic than the parent base. T. A. H.

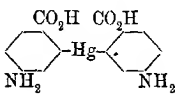
Preparation of Nuclear-substituted Mercury Derivatives of Polysubstituted Phenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 250746. Compare A., 1911, i, 1056; 1912, i, 754).—Organic mercury compounds have previously been prepared (compare Dimroth, A., 1902, i, 656, and *loc. cit.*), and the following more complex derivatives are now described.

The crystalline *compound*, $OH\cdot C_6H_2Me_2\cdot Hg\cdot OAc$, is obtained when 12 parts of *p*-xylenol (A., 1878, ii, 410) dissolved in methyl alcohol are treated with mercuric acetate (30 parts) in water (100 parts) and gently warmed until the addition of an alkaline hydroxide ceases to precipitate mercuric oxide.

Similar *compounds* from creosol, pyrogallol 1:3-diethyl ether (A., 1878, ii, 869), and from bromo-*p*-xylenol (A., 1878, ii, 410) are described in the original. F. M. G. M.

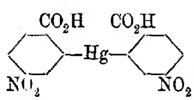
Preparation of Derivatives of Aminobenzoic Acid and its Salts Containing Mercury in the Ring. VEREINIGTE CHEMISCHE WERKE AKTIENGESELLSCHAFT (D.R.-P. 249725).—When the mercury salts of *o*-, *m*- or *p*-nitrobenzoic acid are heated during some hours at about 225°, the mercury becomes attached to a ring carbon atom; these *nitro*-compounds can then be reduced to the corresponding amines.

pp-*Diamino*-oo'-*mercuridibenzoic acid* (annexed formula), a colourless (to yellow) crystalline powder, is obtained by reducing the nitro-compound with ferrous sulphate in alkaline solution; the crystalline *hydrochloride* can be isolated by means of alcohol. The *barium*, *calcium*, *silver*, and *lead* salts are precipitable; the nickel salt gives a greenish-blue, and the iron salt a brown, solution; the green solution of the copper salt becomes brown when boiled, a characteristic which distinguishes it from the solution of the copper salt of the nitro-compound, which is blue and unaffected by boiling.



The ortho- and meta-compounds have similar reactions, and are obtained by the same method; or the mercury salt can be replaced by other salts of aminobenzoic acids, which are then heated with a salt of mercury. F. M. G. M.

Preparation of Dinitrodiphenylmercuridicarboxylic Acids. VEREINIGTE CHEMISCHE WERKE AKTIEN GESELLSCHAFT (D.R.-P. 251332. Compare preceding abstract).—A further account of the preparation of *pp*-dinitro-*oo'*-mercuridibenzoic acid, in which a catalyst, such as stannous chloride or ferrous hydroxide, is employed to assist the condensation; together with the preparation and properties of the *sodium*, *silver*, *barium*, *nickel*, and *cobalt* salts.



mm'-Dinitro-*oo'*-mercuridibenzoic acid and its *sodium*, *silver*, *barium*, *nickel*, and *iron* salts are also described; the salts of these compounds are extremely poisonous, and possess a powerful therapeutic action. F. M. G. M.

Preparation of Esters of Aromatic Carboxylic Acids containing Mercury and their Products of Hydrolysis. WALTER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 248291. Compare A., 1912, i, 754).—When glycyl salicylate (182 parts) and mercuric acetate (318 parts) are boiled together during several hours in methyl-alcoholic solution, a crystalline *ester*, m. p. 165—170° and containing 15·5% Hg, is obtained, which, on hydrolysis, furnishes a compound identical with "hydrargyrum salicylicum." Methyl anthranilate (165 parts) under similar conditions furnishes a *product*, m. p. 191°, containing 47·28% Hg, and on hydrolysis an inner *anhydride* containing 57·3% mercury; whilst *iso*butyl *p*-aminobenzoate yields a *compound*, m. p. 208° (decomp.), with mercury content 44·24%, and an *anhydride* containing 59·51% Hg.

The *phenyl glycyl* ester has m. p. 128—131°, contains 45·9% Hg, and the corresponding *anhydride* has 57·3% Hg. F. M. G. M.

Physiological Chemistry.

The Regulation of Neutrality by the Respiratory Centre, and its Stimulability in Maintaining the Carbon Dioxide Tension of the Blood. KARL A. HASSELBALCH (*Biochem. Zeitsch.*, 1912, 46, 403—439).—The conception underlying these investigations is the following: The magnitude of the lung ventilation is regulated by the magnitude of the stimulus and the stimulability of the breathing centre. The stimulus is the excess of the hydrogen-ion concentration above normal of the blood. A given magnitude of stimulus will cause a greater ventilation of the lungs the greater the stimulability of the centre, and vice versa. The C_H of the blood will alter therefore in the inverse ratio to the stimulability of the centre. This theory was tested in the following way: Considerable changes in the C_H of the urine were brought about on normal individuals by changes in the diet. The magnitude of the changes thus caused were greater than deviations from the normal found in pathological urine. The effect of such a change was to cause a change in the tension of the alveolar carbon dioxide in an opposite direction. It was experimentally shown, furthermore, that the changes in diet did not affect the stimulability of the centre. This fact was ascertained by measuring the effect on the respiration of breathing increased quantities of carbon dioxide. It was further found that the C_H of the blood (measured under a constant carbon dioxide tension) altered under varying conditions of diet, in the

same direction as the C_H of the urine. The alveolar carbon dioxide tension appears to alter in such a way that the actual C_H of arterial blood (measured under the same carbon dioxide tension as exists in the arteries) remains a constant under the varying conditions. The theory is supported by experiments in which the stimulability of the centre was artifically diminished (as, for example, by morphine) or increased. S. B. S.

Absence of Apnœa After Forced Breathing. WALTER M. BOOTHBY (*J. Physiol.*, 1912, **45**, 328—337).—In some persons, forced breathing is not followed by apnœa; the loss of carbon dioxide consequent on forced breathing is made up within a few minutes, but not so rapidly as when apnœa occurs. This exceptional condition is probably due to a compensating diminution of the circulation through the respiratory centre, in consequence of which the gas tensions in the centre are still capable of exciting it. W. D. H.

The Differences in Composition between Arterial and Venous Blood. HUGO WIENER (*Zeitsch. physiol. Chem.*, 1912, **82**, 243—265).—The total protein in the blood of the renal vein is less than in that of the carotid artery and femoral vein (dog). Venous blood is relatively rich in globulin, but this is not so marked in the blood of the renal vein. In nephritis, the reverse obtains.

W. D. H.

Distribution of Sodium and Potassium in the Animal Organism. P. J. GÉRARD (*Chem. Zentr.*, 1912, ii, 846—847; from *Bull. Sci. pharm.*, 1912, **19**, 265—283).—In three successive venesections, the ratio K : Na in rabbit's blood varied between 0·68 and 0·61. The sodium in contrast to the potassium remained constant, deficiences of the former being replaced by sodium withdrawn from the tissues. The ratio was also determined in various marine and land animals, and in various secretions. The author, when working with mice and frogs, was unable to confirm the antagonistic action of sodium salts on the toxic action of potassium salts, as demonstrated by Loeb in the case of *Fundulus*. The toxic action of potassium depends to a large extent on the concentration of the solution employed. S. B. S.

The Influence of Nitrogenous Metabolism Products which Occur Naturally in Blood and Urine on the Blood Pressure. E. LOUIS BACKMAN (*Chem. Zentr.*, 1912, ii, 624; from *Zentr. Physiol.*, 1912, **26**, 166—169).—Urea in from 2—10% solutions in saline caused a rise of blood-pressure (maximum 26 mm. mercury) when injected into rabbits. Ammonium carbamate in 0·5% solution caused a lasting rise, whereas in 0·1% solution it exerted no action. Ammonium carbonate in 0·6% solution caused a lowering of blood-pressure (maximum 38 mm.), but in 0·1% solution a lasting rise. Six % ammonium hippurate caused a transient rise (9 mm.), followed by a lowering. Three % solutions caused a slight rise. Creatine, hypoxanthine, and sodium urate caused lasting rises. Allantoin in

2% solution caused a lasting rise (maximum 5 mm.), and in 1% also a rise after a considerable latent period. Urea also exerts an influence on the heart beats. A mixture of 2% urea, 0·05% ammonium carbamate, 1% sodium hippurate, 1% creatine, 0·2% hypoxanthine, 0·01% xanthine, 0·03% sodium urate causes a large (maximum 46 mm.) and long lasting rise, but has small influence on the frequency of the heart beat. The investigations indicate that nitrogenous metabolism products exert an autoregulatory function in the organism, and their action explains certain pathological conditions in gout and nephritis.

S. B. S.

The Part Played by the Suprarenals in the Normal Vascular Reactions of the Body. G. VON ANREP (*J. Physiol.*, 1912, **45**, 307—317).—Stimulation of the splanchnic nerves causes a rise of blood-pressure, which occurs in two phases. The second phase is accompanied by constriction of peripheral blood-vessels (even after denervation) and by increased cardiac activity (also after denervation). This second rise is due to discharge of adrenaline into the circulation, and is absent after extirpation of the two suprarenal glands.

W. D. H.

Local Vascular Reactions and their Interpretation. G. VON ANREP (*J. Physiol.*, 1912, **45**, 318—327).—The contraction of blood-vessels, described by Bayliss as a local reaction of the vessel wall to increased internal pressure, is due to the action of adrenaline, the secretion of which is increased under the conditions of his experiments. The dilatation of blood-vessels, ascribed by Bayliss to lowering of internal pressure, is due to the direct action on the vessel walls of asphyxial products.

W. D. H.

Glycolysis. III. The Influence of Glycine and Boric Acid Anions on the Oxidative Destruction of Dextrose in the Presence of Phosphates. WALTHER LÖB and S. GUTMANN (*Biochem. Zeitsch.*, 1912, **46**, 288—295. Compare A., 1911, ii, 504).—It has been already shown that phosphate mixture accelerates the destruction of dextrose by hydrogen peroxide. This is not due to the neutrality of the medium, but is specific for phosphates, as no acceleration takes place when neutral borate or other mixtures of the same hydrogen-ion concentration are employed. The authors now show that the addition of such a borate mixture to the phosphate mixture exerts no very marked action, whereas a similar glycine mixture (prepared according to Sörensen) exerts a marked inhibitory action on the glycolysis.

S. B. S.

The Significance of Proteolysis in Specific Hæmolysis. KOHSHI OHTA (*Biochem. Zeitsch.*, 1912, **46**, 247—252).—An immune serum (sheep's blood into rabbit) hæmolyses the specific blood (of sheep) without any proteolysis.

S. B. S.

The Influence of the Hydrogen-ion Concentration on Specific Precipitin Reactions. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1912, **47**, 59—72).—The forma-

tion of specific precipitins and agglutins is, within wide limits, independent of the hydrogen-ion concentration. This factor only comes into play, to any extent, when the reacting substances are in very dilute solutions. In this respect, the precipitin reaction differs from the non-specific precipitation of colloids, as no optimal conditions for precipitin reaction, analogous to the isoelectric point, could be discovered. These results indicate that there is some specific chemical affinity coming into play, and the electric charge of the particles plays only a subordinate part. S. B. S.

The Coagulation of Blood. Ernst Fuld and Erich Schlesinger (*Chem. Zentr.*, 1912, ii, 1569; from *Berlin klin. Woch.*, 1912, 49, 1323—1327).—Dialysis of the blood against an isosmotic salt solution deprives the plasma of its power of coagulating, the crystalloid which is removed being the calcium salt of fibrin. The absence of this salt also hinders the formation of another necessary element in coagulation, namely, the fibrin ferment, for the development of which, cytothrombin from the cells and plasmothrombin from the plasma are also necessary. The injection of cytothrombin into a vein at once causes coagulation, owing to the formation of this ferment, *neothrombin*. The smallest amounts of enzymes would soon set up fermentation processes, which would hinder the circulation, were there not also present substances which prevent coagulation.

Fibrin may be redissolved by fibrinolysis, which is partly due to salt action and also to an enzymatic agent, *thrombase*. J. C. W.

The Dissociation of Oxyhæmoglobin in Human Blood During Partial Carbon Monoxide Poisoning. J. B. S. Haldane (*Proc. physiol. Soc.*, 1912, xxii–xxiv; *J. Physiol.*, 45).—The presence of carboxyhæmoglobin in the blood delays the dissociation of the oxyhæmoglobin present, so that even though the amount of oxyhæmoglobin may be half the normal (as it may also be in a man with anæmia without grave results), the combination of the remaining half of the hæmoglobin with carbon monoxide produces a serious state of affairs. W. D. H.

Blood-relationships of Animals as Displayed in the Composition of the Serum-proteins. I. A Comparison of the Serum of the Horse, Rabbit, Rat, and Ox in the Normal and Fasting Condition. T. Brailsford Robertson (*J. Biol. Chem.*, 1912, 13, 325—340).—The amounts of insoluble globulin, total globulin, and total albumin in serum were determined by the author's refractometric method. In the rabbit the results agree with those arrived at by others in other ways. Horse serum yields not more than 40% of the total albumin in crystalline form. In fully fed animals the three groups of proteins vary greatly; but the average values are characteristic of the species. In fasting, the total protein is also highly variable; in starvation it rises. In rabbit, ox, and horse, inanition increases the relative amount of albumin, whereas in rat and dog the reverse obtains. W. D. H.

The Diastatic Action of Human Saliva. GOICHI HIRATA (*Biochem. Zeitsch.*, 1912, **47**, 167—183).—The diastatic value of saliva (as determined by Wohlgemuth's method) remains practically constant throughout the day, and is not influenced by the time of meals or the diet. The value is also independent of the amount of saliva secreted, and of the age or sex of the individual. It has the same value in certain pathological cases investigated as in normal cases, and appears to be uninfluenced by the hæmoglobin content of the blood. In the case of the Japanese, it varies between $D^{38°}_{30'}$ 160 and 640 in different individuals. S. B. S.

Formation of Hydrochloric Acid in the Stomach. J. LÓPEZ-SUÁREZ (*Biochem. Zeitsch.*, 1912, **46**, 490—499).—The author discusses the evidence as to the acid-secreting function of the oxyntic cells of the stomach, and considers that this has not been demonstrated. By direct chemical analysis he shows that the mucous membrane of the fundus contains more chlorine than that of the pylorus. He shows, furthermore, by Macallum's histological method that the ordinary cells contain more chlorine than the oxyntic cells. S. B. S.

The Fat-hydrolysing Ferment in Gastric Juice, and its Estimation. HEINRICH DAVIDSOHN (*Chem. Zentr.*, 1912, ii, 1378—1379; from *Berl. klin. Woch.*, 1912, **49**, 1132—1134).—Rona and Michaelis's drop method for following the course of butyrin hydrolysis (A., 1911, ii, 302) has been applied to a large number of gastric juices, and a widely varying enzyme action has been observed. Directions are given whereby the method may be applied to the estimation of this hydrolytic enzyme. J. C. W.

Tryptic Digestion of Cynoscion regalis. GEORGE F. WHITE and ADRIAN THOMAS (*J. Biol. Chem.*, 1912, **13**, 111—116).—The flesh of *Cynoscion regalis*, an American fish known commonly as the weakfish or squeteague, was subjected to tryptic digestion in vitro, and the amino-acids in the digest were determined by Sörensen's formaldehyde method. The results were regular and in accord with those obtained by van Slyke's nitrous acid method for estimating amino-nitrogen. The relatively low rate at which the protein becomes soluble agrees with the results of metabolism experiments. Very low cleavage products are formed as soon as the protein passes into solution, the average size of the peptides being 2·02 after half an hour's digestion; but there is a very stable nitrogen complex which is not attacked by trypsin. W. D. H.

Animal Calorimetry. V. The Influence of the Ingestion of Amino-acids on Metabolism. GRAHAM LUSK and J. A. RICHE (*J. Biol. Chem.*, 1912, **13**, 155—184. Compare A., 1912, ii, 1189).—After giving meat, the metabolism of the dog during the second hour rose almost to a maximum, and the respiratory quotient was 0·9; it therefore appears that carbohydrate and not additional protein is oxidised during this period. After the ingestion of amino-acids and especially of glycine, there is a similar increase in the metabolism;

this can have nothing to do with deamidation or urea-formation, but is attributed to a direct stimulating action of the amino-acids on the cells of the body. A mixture of five amino-acids produced a more rapid metabolism than when given singly, and more than meat containing the same amount of nitrogen. W. D. H.

Animal Calorimetry. VI. The Influence of Mixtures of Food-stuffs on Metabolism. GRAHAM LUSK and J. A. RICHE (*J. Biol. Chem.*, 1912, 13, 185—208).—Further details are given of the effect of diet on metabolism, and the conception of the process put forward is that to a basal metabolism (at rest) there may be added metabolism due to plethora, that is, an increased supply of fats and carbohydrates, or the superadded metabolism may be due to the stimulus of amino-acids. When these two are added to each other there is no summation of effects. W. D. H.

Fatty Acid Metabolism in the Liver. II. The Relation of the Fatty Acids in the Food of the Plaice to those in their Livers and Myotomes. V. H. MOTTRAM (*J. Physiol.*, 1912, 45, 363—369).—The fatty acids of the mussel have a high iodine value, which falls between that of the fatty acids of the liver and those of the myotomes of the plaice. Such fatty acids are therefore not characteristic of the vertebrates, and they occur before the appearance of a true liver. Their formation is not exclusively a liver function. The experiments on the feeding of plaice on mussels cannot, however, be considered a refutation of Leathes' theory of the desaturating influence of the liver in fatty acid metabolism. W. D. H.

The Biochemical Synthesis of Fatty Acids from Carbohydrates. IDA SMEDLEY (*Proc. physiol. Soc.*, 1912, xxv—xxvii; *J. Physiol.*, 45).—Various hypotheses to explain the conversion of carbohydrate into fat are discussed. Although pyruvic and other α-keto-acids have not yet been detected in the tissues, the theory is favoured that pyruvic acid is an intermediate product. W. D. H.

Maintenance Experiments with Isolated Proteins. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem.*, 1912, 13, 233—276).—Details are given and general questions discussed on the nutrition of white rats for long periods on foods containing a single purified protein. With the precautions described this is possible, and they can be so maintained for periods equal to their adult lives. This is true for gliadin, edestin, and casein, which are proteins of very different composition. As glycine is absent from casein, lysine and glycine from gliadin, and phosphoproteins from gliadin and edestin, and purines throughout are practically absent, the synthetic activities of the animal body are clearly brought to mind. The possibilities of transmutation of amino-acids must be considered, and the view that proteins as near as possible in constitution to those in an animal's body are most nutritious must be regarded with caution. Long-continued experiments are necessary in all such work. Changes in the nitrogen balance over short periods may be entirely deceptive. W. D. H.

The Influence of Lecithin on the Nitrogen and Phosphorus Balance. ALDO PATTA (*Chem. Zentr.*, 1912, ii, 939—940; from *Arch. Farm. sperim.*, 1912, 13, 515—528).—Small quantities of lecithin (0·05 to 0·10 gram) administered subcutaneously to a dog scarcely altered the nitrogen and phosphorus metabolism when there was a small deficit in these substances. Larger doses (0·5 to 0·75 gram) caused a sparing action, which was small when the nitrogen and phosphorus ingested were insufficient, but was marked when these elements were in excess of the body needs. The sparing action of the phosphorus was larger than the amount injected as lecithin, and the fact that the injection caused an increase of the nitrogen in the urine, at the expense of the fœcal nitrogen, indicates that the lecithin stimulates the degradation of the injested proteins. S. B. S.

Retention of Nitrogen after Feeding on Ammonium Salts. E. GRAFE (*Zeitsch. physiol. Chem.*, 1912, 82, 347—376).—The present experiments on pigs confirm those previously recorded on dogs (A., 1912, ii, 659). Administration of ammonium salts mixed with abundance of carbohydrate leads to nitrogenous equilibrium, or even a retention of nitrogen. W. D. H.

The Creatine Metabolism of the Growing Pig. ELMER V. McCOLLUM and H. STEENBOCK (*J. Biol. Chem.*, 1912, 13, 209—218).—In some animals (for instance, the rabbit) fasting causes the appearance of creatine in the urine. In dogs, depletion of the liver of glycogen leads to the same result, and Mendel and Rose (A., 1911, ii, 1002, 1007) consider that there is a definite relationship between creatine and carbohydrate metabolism; they further think that creatine is not a result of exogenous protein metabolism, but only of endogenous metabolism. The present experiments on pigs were planned to investigate this question, but it was found that in this animal fasting does not lead to the appearance of creatine in the urine; this is explained in differences of metabolic habit. When a rabbit fasts the total nitrogen excreted rises, indicating an increase of protein katabolism. This does not happen in the dog, or only slightly, and not at all in the pig. The pig is an efficient fat-storer, so he might be expected to use it readily for energy production. On an uniform diet considerable irregularities in the excretion of creatine occur, and the idea that creatine is destroyed by enzymes is supported. Data are also given which leave but little doubt that creatine may arise from exogenous as well as from endogenous protein metabolism, and that its source, or one of its sources, is arginine, is regarded as probable. W. D. H.

The Behaviour of Some Hydantoin Derivatives in Metabolism. I. Hydantoin and Ethyl Hydantoate. HOWARD B. LEWIS (*J. Biol. Chem.*, 1912, 13, 347—356).—After hydantoin is given, an insoluble benzylidenehydantoin can be recovered from the urine, which accounts for only part of the hydantoin administered. No toxic effects follow, which is against Lusini's theory of the toxicity of $\begin{matrix}-HN\\-HN\end{matrix}\!\!>\!C{:}O$ groups.

Hydantoic acid, of which hydantoin is the cyclic anhydride, is not destroyed in metabolism when given as the ethyl ester. The hydantoin nucleus is not destroyed in the body of cat, rabbit or dog.

W. D. H.

Purine Metabolism. X. The Property of the Organism to Destroy, or Form by Oxidative Processes, Uric Acid in Animals Capable of Producing this Acid Synthetically. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1912, **47**, 215—225).—In experiments carried out with ducks, it was found that animals which normally synthesise uric acid can also destroy this acid after ingestion when added to a normal diet, to the extent of 33—59% of the total. They can also degrade guanine to xanthine, and into still simpler complexes which no longer contain a purine group. From the xanthine thus formed, a certain amount of uric acid can be formed by an oxidative process. Ingestion of nucleic acid also causes a slight increase in the amount of purine bases execreted and a considerable increase in the uric acid, the origin of which is ascribed to the protein groups.

S. B. S.

The Metabolism of Endogenous and Exogenous Purines in the Monkey. ANDREW HUNTER and MAURICE H. GIVENS (*J. Biol. Chem.*, 1912, **13**, 371—388).—In the urine of the guenon monkey (*Cercopithecus*), allantoin accounts for 75% of the nitrogen arising from the katabolism of endogenous purines. The rest appears principally as purine bases, uric acid being practically absent on a purine-free diet. Allantoin is a true end-product. When purines are given, allantoin is increased, and uric acid appears as an intermediate product. Only 12—54% of total purine intake is accounted for. The deficit is probably due to decomposition prior to absorption. There is no approach in this monkey to the human type of nuclein metabolism.

W. D. H.

Absorption from the Stomach. OTTO FOLIN and HARRY LYMAN (*J. Biol. Chem.*, 1912, **13**, 389—391).—A reply to London's recent criticisms (A., 1912, ii, 1189).

W. D. H.

Behaviour of Intestinal Wall After a Prolonged Period of Functional Inactivity. PAOLO MARICONDA (*Zeitsch. physiol. Chem.*, 1912, **82**, 406—412).—After making a Vella fistula, a dog was kept for several months so that no local stimulus had reached the intestine. The amount of fluid secreted by the intestinal wall was now very small, and the amount of the various enzymes was also reduced, although not to the same extent. The results are opposed to the theory that the secretory function of the intestine is due to chemical stimuli carried to it by the blood. Sucrose introduced into the fistula passes the wall without being changed; the selective absorptive power of the intestinal wall has been destroyed.

E. F. A.

Absorption of Cholic Acid in the Dog's Intestine. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1912, **82**, 342—345).—Experiments with intestinal loops showed that in all probability cholic acid is absorbed unchanged by the intestinal wall.

W. D. H.

The Fate of Deeply-degraded Proteins in the Intestine. PETER RONA (*Biochem. Zeitsch.*, 1912, 46, 307—316).—Experiments were carried out with the object of ascertaining whether any protein synthesis takes place in the small intestine. Pieces of surviving intestine were placed in Tyrode's solution and various digestion products or mixtures of amino-acids were placed either in the solution in which the intestine was kept or introduced directly into the lumen. The experiments were carried out at 38°, and during this time the intestine maintained its peristaltic movements. The amino-nitrogen was estimated both before and after the experiment. There was generally an increase in this nitrogen at the end, due probably to amino-substances given up by the intestine itself. The amount of increase was of the same order as that in which the experiments were carried out in Tyrode's solution without any addition. No evidence was obtained therefore of any synthetical process affecting amino-derivatives in the intestine. S. B. S.

The Investigation of the Permeability and Antagonistic Action of Electrolytes by means of a New Method. JACQUES LOEB (*Biochem. Zeitsch.*, 1912, 47, 127—166).—It has been already repeatedly shown by the author, in experiments on *Fundulus* eggs, that treatment with a solution of one salt alone (for example, sodium chloride) alters the permeability of the membrane, and that this alteration can be inhibited by the addition of certain quantities of another salt (calcium chloride). Salt solutions, of such composition that the antagonistic action of the salts is at its maximum, are designated equilibrated solutions. If fertilised eggs of *Fundulus* be brought into a solution of 50 c.c. $3M$-sodium chloride + 2 c.c. $10/8M$-calcium chloride, they will remain on the surface for three days, after which the membrane will be rendered permeable by the hypertonic solution; the eggs will then begin to shrink, and owing to the passage outwards of water, the specific gravity will increase and they will then sink in the solution. If brought into a solution of $3M$-sodium chloride alone, without presence of calcium chloride, they will sink within three to four hours, and the membrane rapidly becomes permeable. Similar phenomena are observed when the eggs are brought into other corresponding solutions containing only salts. By the method of experiment the various earlier investigations of the author have been confirmed. The changes in the permeability appear to be due chiefly to the proteins, and there is an antagonism between the action of acids and the corresponding salts, which is characteristic of proteins, as Pauli and his pupils have shown. Furthermore, the antagonism in the system H_2SO_4–Na_2SO_4 is more complete than in the system HCl–NaCl. The antagonistic action of these acids and salts on the *Fundulus* egg, as studied by the method described above, confirms the theory as to the alterations of the proteins by salts. The quantitative study of the action of alcohols, however, indicates that these alter the permeability by the action on the fatty constituents of the membrane. Provided that the action has not gone too far, the change of permeability produced by salts is a reversible one, and eggs, which have been a short time in a toxic

solution, will recover their normal properties when brought into an equilibrated solution. Eggs will also remain alive in distilled water, and fish will develop, but they will not recover their impermeability. If such eggs are brought into a solution of 50 c.c. $3M$-calcium chloride + 2 c.c. $10/8M$-calcium chloride, they sink in a few hours.

S. B. S.

The Influence of Neutral Salts on Ferment Action. II. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1912, **47**, 300—319. Compare A., 1910, i, 449).—The number of salt molecules necessary to activate to the maximum extent an inactive diastase preparation is proportional to the amount of ferment. This fact suggests a process for the determination of the quantity of ferment in a given organ. For this purpose the organ is dried, a 5% suspension of the dried powder is made up, and dialysed. The amount of salt which produces the maximum diastatic effect with this fluid can then be ascertained. By this means the diastase content in various animal organs was investigated. Organs of warm-blooded animals contain more ferment than those of the cold-blooded. The ferments obtained from both kinds of animals work more rapidly at higher temperatures.

S. B. S.

Lipoids. XVI. The Cholesterol Content of Different Parts of the Brain. SIEGMUND FRÄNKEL, P. KIRSCHBAUM, and KURT LINNERT (*Biochem. Zeitsch.*, 1912, **46**, 253—256).—The cholesterol was estimated as its digitonin derivative. In a human brain 4·03% was found in the pons and medulla oblongata, 2·47% in the white matter of the cerebrum, and 1·31% in the cerebellum.

S. B. S.

The Colloidal Structure of Nerve Cells and the Changes which they Undergo. G. MARINESCO (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 209—225).—The ultra-microscopic structure of nerve cells is described and interpreted on the assumption that the cell constituents are of colloidal character. The structural changes which are observed when the nerve cells are subjected to the action of acids, alkali, salts, and various other substances, such as ethyl alcohol, carbamide, glycerol, sucrose, chloral hydrate, and antipyrine, are also described in detail.

The results of these ultra-microscopic observations seem to show that the particular structures which are presented by the nerve cells after treatment by the usual fixing and colouring methods are essentially determined by the nature of the histological processes employed. The fixing reagents have, in general, a coagulating effect on the colloidal cell constituents, and the observed facts agree with the view that the protoplasm is a negative colloid.

H. M. D.

Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions. IV. The Chemical Composition of the Brain in Progressive Paralysis. DOMENICO CARBONE and GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1912, **46**, 450—469).—The analyses of brains taken from

individuals who have suffered from progressive paralysis and Dementia præcox paraxoica were compared with those obtained from mentally normal individuals. Whereas normal brains contain about 23% of dry substance, those from mentally afflicted (five cases) varied between 17 and 21%. Against a normal value of 20%, the acetone extracts of the abnormal brains varied between 22·87% and 31·32%. The light petroleum extracts varied between 11·23% and 23·14%, as compared with the amount from normal brains of 27·84%. The cholesterol varied between 13·9 and 24·2%, and the other extractives between 4·5 and 11·84% as compared with the normal values of 10·96 and 9·64%. Full details as to analytical methods are described by the authors. S. B. S.

Broncho-dilator Nerves. Walter E. Dixon and Fred Ransom (*J. Physiol.*, 1912, **45**, 413—428).—The broncho-dilator nerves are of sympathetic origin. Adrenaline given to an animal showing bronchial tonus causes active temporary dilatation; atropine causes passive permanent dilatation. W. D. H.

The Influence of Inorganic Salts on the Perfused Heart. W. Burridge (*Quart. J. expt. Physiol.*, 1912, **5**, 347—372).—Potassium salts give rise to two types of contraction in cardiac muscle (frog), which are termed "tonic contraction" and "contraction effect." Some salts produce one, others the other effect, but all temporarily abolish rhythmical activity, and may produce "heart block" if perfused at high pressure. The effects are mainly explained by considering that these salts displace calcium salts, and the various calcium salts are displaced at varying rates. Seasonal variations noted are explained as due to changes in the balance between calcium and potassium salts in the heart muscle; temperature may also be a factor. W. D. H.

Physiology and Pharmacology of the Cardiac Vagus. I. The Influence of Chloral Hydrate on the Result of Vagus Stimulation. Otto Loewi (*Arch. expt. Path. Pharm.*, 1912, **70**, 323—342).—Intravenous injection of chloral hydrate in small doses has no effect on blood pressure and heart rate, but almost completely annuls the return of the heart-beat during vagus stimulation. Large doses abolish vagus excitability. Camphor has also no effect on blood-pressure or pulse rate, but influences vagus stimulation in a similar way. The action of pilocarpine and muscarine is similarly weakened. W. D. H.

Physiology and Pathology of the Cardiac Vagus. II. The Importance of Calcium for Vagus Action. Otto Loewi (*Arch. expt. Path. Pharm.*, 1912, **70**, 343—350).—Partial removal of calcium by small amounts of oxalate increases the excitability towards electrical stimuli of various nerves; the least affected is the pelvic nerve, but the chorda tympani and especially the vagus are profoundly affected. This is not inhibited by calcium. The action of muscarine on the frog's heart occurs after it is rendered poor in calcium,

or free from calcium. The paralysis of the vagus by pilocarpine or muscarine in mammals and frogs is not influenced by calcium.

W. D. H.

Physiology and Pharmacology of the Cardiac Vagus. III. Vagus Excitability and Vagus Poisons. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, **70**, 351—368).—In very small doses muscarine (and pilocarpine) increases vagus excitability in the frog. In vagus paralysis produced by these drugs there exists neither in frog nor rabbit any automatic ventricular action. The effect of prolonged electrical stimulation of the nerve is either increased by muscarine or unaffected by it, according to the duration of the stimulation or the dose of the poison. Similarly, the pilocarpine effect can be superposed on the muscarine effect, or vice versa. Physostigmine does not sensibilise the muscarine or pilocarpine action. The action of pilocarpine and muscarine is considered to be on the myoneural junction.

W. D. H.

The Behaviour of Acetic Acid in the Artificial Perfusion of the Liver. ADAM LOEB (*Biochem. Zeitsch.*, 1912, **47**, 118—126).—Various results obtained by Embden and his school are recapitulated, and reasons are given as to why acetic acid might be expected as a normal degradation product of fats, carbohydrates, and proteins, especially through the intermediation of pyruvic acid. As no evidence could be obtained of the formation of acetic acid when pyruvic acid was added to blood in a perfusion experiment, the effect of adding the former acid itself to the blood was investigated. It was found that, during perfusion, a very marked disappearance of this acid took place. It was also found, without exception in ten experiments, that the addition of acetic acid to the perfusion of blood caused a marked increase in the formation of acetoacetic acid. The mechanism of this reaction is discussed, and it is provisionally suggested that the degradation of acetoacetic into acetic acid is a reversible process:

$$CH_3\cdot CO\cdot CH_2\cdot CO_2H \rightleftarrows 2CH_3\cdot CO_2H,$$

and for this reason the acetic acid may inhibit the degradation of the acetoacetic acid normally formed to simpler products.

S. B. S.

The Fate of Glyoxylic Acid in the Animal Body. GEORG HAAS (*Biochem. Zeitsch.*, 1912, **46**, 296—306).—On incubation of minced liver of various animals with glyoxylic acid, this substance partly disappeared, but no definite degradation products were isolated. Its perfusion through rabbit's liver gave rise to formic acid, and this acid could also be isolated in the urine of a dog which had received glyoxylic acid *per os*.

S. B. S.

The Destruction of Alkaloids by the Body Tissues. A. J. CLARK (*Quart. J. expt. Physiol.*, 1912, **5**, 385—398).—The liver of frog and rabbit possesses the power of destroying atropine; this persists after the cells are destroyed, and is due to a soluble substance resembling an enzyme in its action. The heart and kidneys of the frog and the

blood of the rabbit have the same power in a less degree, but all the other tissues are destitute of the power. None of the tissues in cat, rat, and dog has the power, and the minimal lethal dose of atropine is highest in those animals the livers of which can destroy it.

W. D. H.

The Distribution of Nitrogen in Autolysis, with Special Reference to Deaminisations. GERTRUDE D. BOSTOCK (*Bio-Chem. J.*, 1912, **6**, 388—415).—The following nitrogen fractions in the autolysis products of liver were determined: ammonia, amide nitrogen, and amino-acid nitrogen. It was necessary to ascertain these factors in order to determine the fate of ammonium salts and amino-acids when digested with liver tissue. In fresh liver the soluble nitrogen fraction is characterised by its low ammonia and amino-nitrogen content. The latter, however, increases after forty-eight hours' incubation at the expense of the undetermined nitrogen fraction. The rate of autolysis reaches its maximum within this period. Acids stimulate and alkalis depress the autolysis rate, and the distribution of nitrogen differs under these two conditions. Acids cause a lower and alkalis a higher percentage of ammonia and undetermined nitrogen fractions than in the control autolyses without addition of either acid or alkali. The reverse is the case with regard to the amide or amino-acid nitrogen. Putrefactive organisms cause a higher percentage of ammonia and undetermined nitrogen. No evidence could be obtained of the formation of amide nitrogen from ammonium sulphate or lactate when digested with liver pulp. There is also no evidence of liberation of ammonia from glycine. In view of the formation of ammonia by putrefactive organisms, any statements as to the liberation of this substance from amino-acids when digested with tissues must be received with caution.

S. B. S.

The Permeability of the Kidneys to Sugar after Repeated Injections of Adrenaline. ARTUR VON KONSCHEGG (*Arch. expt. Path. Pharm.*, 1912, **70**, 311—322).—Diuresis which follows the injection of adrenaline is independent of glycosuria. After salt diuresis is produced, it is not possible to produce glycosuria by such injections; the blood contains no excess of sugar, but the kidneys themselves contain more than normal. Inhibition of glycosuria is not brought about by the kidneys being unable to take up sugar from the blood.

W. D. H.

The Amount of Silicic Acid in Human Thyroid Glands. HUGO SCHULZ (*Biochem. Zeitsch.*, 1912, **46**, 376—392).—The mean content of the normal glands from the neighbourhood of Greifswald was 0·0084%, and that of pathological glands from the same district, 0·0175%. The pathological glands from Zürich, on the other hand, contained as much as 0·0434%. The author, nevertheless, gives reasons for not believing that goitre is due to water containing silicic acid, and he failed to produce the disease experimentally in animals which had received over long periods water containing relatively large quantities of the acid.

S. B. S.

The Creatine-splitting Enzyme of the Parathyroids and the Suprarenals. ALBERT HOLMES ROWE (*Amer. J. Physiol.*, 1912, 31, 169).—A creatine-splitting enzyme is present in the thyro-parathyroid tissue; this confirms the results of Gottlieb and Stau-gassinger. A similar enzyme is found in suprarenal extract. There is no evidence that either the parathyroids or the suprarenals contain a creatine-splitting enzyme which can be activated by the other.

W. D. H.

The Chemistry of Normal and Eclamptic Placenta. L. MOHR and W. HEIMANN (*Biochem. Zeitsch.*, 1912, 46, 367—373).—Estimations were made of the water content, total phosphoric acid and nitrogen, ether soluble substances, cholesterol, neutral fat, and diastearyllecithin. The last-named was appreciably larger in normal placenta than in cases of eclampsia. There was no marked difference in the other factors.

S. B. S.

The Physico-chemical Basis of a Theory of Muscular Contraction (Zuntz's Theory). WILLIAM N. BERG (*Pflüger's Archiv.* 1912, 149, 195—220. Compare A., 1912, ii, 1077).—A critical and antagonistic discussion of Zuntz's theory; the main point is that lymph contains practically no carbon dioxide in the simple gaseous condition, and that when gases are dissolved in water they behave differently from substances in true solution, and, with the exception of hydrogen chloride and ammonia, exert no osmotic pressure. The carbon dioxide which is formed by muscular activity has therefore no osmotic pressure.

W. D. H.

The Anaphylactic Reaction of Plain Muscle in the Guinea Pig. HENRY H. DALE (*Proc. physiol. Soc.*, 1912, xxvii—xxix; *J. Physiol.*, 45).—Experiments on the plain muscle (uterus) of the guinea pig sensitised to horse-serum and other proteins; it reacts in response to minute doses (one in a million) of the specific antigen; after response it is completely desensitised; it can be re-sensitised by soaking in the serum of sensitised guinea pigs. The time relations of the reaction exclude the production of a poison by parenteral digestion. The antigen acts on the sensitised muscle like a stimulant drug, the peculiar feature being that the "receptive or anti-substance" is detachable. There is much evidence in favour of the view that the anaphylactic anti-substance is identical with precipitin. W. D. H.

Synthesis of Lecithin in the Hen and the Character of the Lecithins Produced. ELMER V. MCCOLLUM, J. G. HALPIN, and A. H. DRESCHER (*J. Biol. Chem.*, 1912, 13, 219—224. Compare A., 1912, ii, 368).—Further experiments are given to show that hens fed on a diet free from lipoids produce eggs which contain lecithin or lecithins. These differ in the nature of their fatty acid radicles, and variation may be produced by the nature of the lipoids of the diet.

W. D. H.

Red Colouring Matter of Boiled Crabs. EUGÈNE GRANDMOUGIN (*Chem. Zeit.*, 1912, 36, 1377—1378).—The change of colour observed

when crab-shells are boiled has been attributed by Kornfeld to the formation of alizarin-red, which depends on the presence of alizarin and aluminium oxide in the unboiled shell.

The author points out that the presence of anthraquinone in the normal organism has not previously been observed. He also finds that the colouring-matter of crab- and lobster-shell, unlike alizarin-red, is soluble in alcohol or ether, and is very sensitive to light. When dissolved in alcohol, it shows characteristic absorption bands in the green portion of the spectrum which differ completely from the bands given by alizarin. It possesses no dyeing power. Finally, the presence of compounds of aluminium in the shell could not be detected with certainty.

The exact nature of the colouring matter has not been determined, but the presence of anthraquinone derivatives is extremely improbable.

H. W.

The Bio-chemistry of Termites. The Chemical Composition of the Fæcal Stalactites of Entermes monoceros. KONRAD SCHÜBEL (*Arch. expt. Path. Pharm.*, 1912, 70, 303—310).—The tree ant of Ceylon protects its nest by so-called stalactites, and it has been surmised that these contain cantharidin or some similar poison. The present work shows that the material consists of an organic non-toxic substance with a small amount of inorganic salts. The ash has the following percentage composition: SiO_2, 45·2; P_2O_5, 1·09; $Fe_2O_3 + Al_2O_3$, 23·5; Mn_3O_4, 1·05; CaO, 14·25; MgO, 1 5, and $K_2O + Na_2O$, 13·3. By distillation in a vacuum it was proved that the fæcal matter contains preformed an olefine, probably $C_{35}H_{70}$, m. p. 75°. These animals live almost exclusively on flies and algæ. W. D. H.

Metabolism Studies on the Cold-blooded Animals. I. The Urine of the Fish. W. DENIS (*J. Biol. Chem.*, 1912, 13, 225—232).—The urine of the dog-fish is clear, odourless, and almost colourless; it is acid to litmus. It darkens and becomes cloudy when kept. It gives the murexide reaction, and contains creatinine, but not creatine. The following is the average composition, expressed in grams per litre: total nitrogen, 4·2; urea nitrogen, 3·4; ammonia nitrogen, 0·3; chlorides (as NaCl), 12·8; phosphates (as P_2O_5), 4·5; total sulphur (as SO_3), 7·1, and total sulphates (as SO_3), 3·4. The goose fish (*Lophius piscatorius*) is the only teleost so far investigated; in general appearance and reaction, the urine resembles that of the dog-fish; uric acid, creatine, and creatinine were absent. The one specimen examined contained, in milligrams per litre, total nitrogen, 400; urea nitrogen, 248, and ammonia nitrogen, 2. W. D. H.

Behaviour of Alicyclic Compounds in Coupling with Glycuronic Acid in the Organism. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1912, ii, 854—856; from *Skand. Arch. Physiol.*, 1912, 27, 141—226).—A number of terpenes and allied compounds dissolved in olive oil were fed to rabbits. The urine produced was collected, and the coupled glycuronic acids formed were either isolated or the products of their hydrolysis by acids were examined.

Menthene in this way gave rise to a product which on hydrolysis yielded a *hydrocarbon*, $C_{10}H_{16}$, b. p. 178—180°, that on hydration gave a dihydric *alcohol*, $C_{10}H_{20}O_2$, m. p. 55—59°, which may be *p*-menthan-2:4-diol. Dihydrocarveol in the same way yielded a menthadiene, $C_{10}H_{16}$, b. p. 179—181°, which on oxidation gave dihydrocarvone, and on hydration furnished *p*-menthan-2:8-diol. Terpin yielded a menthadiene, b. p. 178—181°, which gave terpin hydrate and terpineol on hydration, and terpenylic acid on oxidation with chromic acid. Menthone, before coupling with glycuronic acid, appears to be oxidised to Δ^4-menthen-3-one, since the latter is produced on hydrolysis of the coupled product.

Thujone is apparently first converted in the organism into *p*-menthan-2-one-4-ol by addition of 1 mol. of water. On hydrolysis the coupled product yields carvenone, whilst oxidation with sodium hypobromite gives ω-dimethyllævulic acid. Thujyl alcohol, under like conditions, seems to be converted into *p*-menthan-2:4-diol, since the latter is formed on hydrolysis of the coupled glycuronic acid produced in the organism.

Sabinol yields *sabinolglycuronic acid*, $C_{16}H_{24}O_7$, m. p. 82—83°, as a colourless, glassy mass, giving crystalline *sodium* and *strychnine* salts. The latter has m. p. 196—197°, $[\alpha]_D^{20}$ − 39·66° in alcohol, and crystallises with $2H_2O$ in needles from hot water. Sabinene yields a coupled product, which on hydrolysis with 5% sulphuric acid gives a gelatinous substance that on hydrolysis with stronger acid yields Δ^1-menthenone (?).

Pinene and nopinene appear to undergo oxidation before coupling, since the coupled product yields *p*-cymene on hydrolysis. Camphane is also oxidised in the organism, and yields a mixture of d- and l-*borneolglycuronic acids*, $C_{16}H_{26}O_7$, m. p. 163—165°, $[\alpha]_D^{20}$ − 56·91°, as a colourless, crystalline mass.

l-Fenchyl alcohol furnishes *fenchylglycuronic acid*, $C_{16}H_{26}O_7,H_2O$, m. p. 124—126°, $[\alpha]_D^{20}$ − 63·07°, crystallising from acetone and yielding well crystallised salts. l-iso-*Fenchylglycuronic acid*, m. p. 140—150°, $[\alpha]_D^{20}$ − 81·02°, is amorphous.

Camphenilolglycuronic acid, $C_{15}H_{24}O_7$, m. p. 150—153°, is a colourless mass, obtained by the use of either camphenilol or camphenilone, the latter apparently undergoing initial reduction in the organism.

α-Santenol gives rise to *α-santenolglycuronic acid*, $C_{15}H_{24}O_7,H_2O$, m. p. 160—161°, $[\alpha]_D^{20}$ − 56·6°, a colourless mass, which yields crystalline salts. *β-Santenol* also couples unchanged, furnishing β-santenolglycuronic acid, which was not isolated, but was found to yield santene on acid hydrolysis. Santenone is first oxidised to *santenonol*, $C_9H_{14}O_2$, m. p. 92—93°, crystallising in colourless leaflets, giving a crystalline *semicarbazone*, m. p. 222—223°, and yielding santenic acid on oxidation. *Santenonolglycuronic acid*, $C_{15}H_{22}O_8$, yields a crystalline *strychnine* salt, $C_{36}H_{44}O_{10}N_2,2H_2O$, m. p. 171—172°, and gives santenonol on hydrolysis.

Camphene hydrate couples unchanged with glycuronic acid in the organism, and the product on hydrolysis gives camphene, by loss of water from the regenerated camphene hydrate. T. A. H.

The Relationships between Tumour Cells and Blood-serum. ERNST FREUND and GISA KAMINER (*Biochem. Zeitsch.*, 1912, **46**, 470—482).—The property possessed by normal sera of destroying carcinoma cells is due to an ether-soluble, nitrogen-free fatty acid. The property of carcinomatous serum of protecting carcinomatous cells from destruction, and of giving specific turbidity with saline extracts of carcinomas, is due to the euglobulin (nucleoglobulin) fraction of the serum which is soluble in sodium carbonate, and is distinguished from normal nucleoglobulin by its high content of carbohydrate group. The property of carcinoma extracts of giving turbidities with carcinomatous sera is due to a nitrogen-free carbohydrate compound. The specific precipitates of carcinomatous and sarcomatous extracts with their respective sera are characterised in the former case by carbohydrate-rich substances, and in the latter case by groups yielding the biuret reaction. The carcinomatous precipitates carry down from solution added carbohydrates, whereas the sarcomatous precipitates carry down added peptone. The tumour cells themselves show a similar adsorptive capacity, the carcinomatous cells binding sugar, lecithin or nuclein, whereas the sarcomatous cells bind peptones and nuclein. S. B. S.

The Interstitial Granules (Liposomes) in Fatty Metamorphosis of Striated Muscle. E. T. BELL (*J. Path. Bact.*, 1912, **17**, 147—159).—Fatty metamorphosis may be produced in the leg muscles of a rat by applying a ligature round the thigh; in the fibres of these muscles the liposomes stain with greater intensity, and are much larger than normal; this is especially the case in well nourished animals, or if the rat is fed on fat. Pathological fatty metamorphosis is an exaggeration of a normal process, and consists in an increase in the size, staining capacity, and often the number of liposomes. Part of the fat is already present when the process begins. The increase of size is probably due to the accumulation of triolein. W. D. H.

Nature of the So-called Klausner Serum Reaction. G. KLAUSNER (*Biochem. Zeitsch.*, 1912, **47**, 36—58).—The author has already shown that sera from certain cases of syphilis yield a precipitate when diluted with three times the volume of water. This property is lost if the serum is previously extracted with ether, and is restored by the addition to the serum of the lecithin–cuorin–cephalin fraction of brain lipoids. A serum can also be rendered non-precipitable by water if heated, but in this case the precipitability (activation) is not restored by lipoids. A serum activated by brain lipoids can also be inactivated by heating. The property of restoring activity by lipoids is not destroyed by heating. An artificially activated serum (by lipoids) if inactivated by heat is not rendered active again by the addition of fresh serum; hence, the activating property of lipoids is best if they are heated in the presence of serum. In all cases both of artificial and natural precipitin reactions, the optimal condition for precipitation is dilution with three times the volume of water. The natural precipitin reaction, when destroyed by heat, is not restored on the addition of fresh serum. A positive serum, inactivated by extraction with ether, can be reactivated

by the addition of the ethereal extract, which can also activate a normal inactive serum. Strong concentrations of the ethereal extracts of normal serum, dissolved in water, can also activate a normal serum. These results indicate that the precipitation is not due to globulins, and that in syphilitic sera the abnormalities are due to excess of lipoids. S. B. S.

Bence-Jones Proteinuria. E. PROVAN CATHCART and J. HENDERSON (*J. Path. Bact.*, 1912, **17**, 238—248).—A detailed account of the examination of the urine in a case of this disease. The general result of an examination of the protein present is that the findings of Hopkins and Savory (A., 1911, ii, 417) are confirmed. W. D. H.

The Action of Carbon Dioxide on the Vascular System. S. ITAMI (*J. Physiol.*, 1912, **45**, 338—344).—Small percentages of carbon dioxide produce a rise of arterial pressure mainly by increasing the force of the heart. Higher percentages (over 8%) produce increased constriction of the arterioles by stimulating the vaso-motor centre, and probably from an increased activity of the suprarenal glands. W. D. H.

Diuretic Action of Mercury Preparations. D. FERRON (*Chem. Zentr.*, 1912, ii, 370; from *Arch. Farm. sperim.*, 1912, **13**, 283—288).—Intravenous injection of doses of 0·000010 to 0·000025 gram-equivalents of mercuric chloride per kilo. of body-weight causes in rabbits an appreciable diuresis, but in larger doses the effect is less than that of the saline injection alone, owing to the toxic properties. A simultaneous injection of sodium chloride decreases the toxic effects, and, vice versa, mercuric chloride diminishes the toxic effects of hypertonic sodium chloride solution. S. B. S.

Action of Mercury Preparations on Spirochaete Diseases. I. Chemical-therapeutic Action of Mercury Compounds, Especially of a New Mercury Preparation which Strongly Attacks Spirochaete, but is only very Slightly Poisonous. WILHELM KOLLE, M. ROTHERMUND, and S. PESCHIĖ (*Chem. Zentr.*, 1912, ii, 1574—1575; from *Deut. med. Woch.*, 1912, **38**, 1582—1585).—The therapeutic action of many mercury preparations, such as colloidal mercury, mercury peptonate, dinitromercuridibenzoic acid, sulphaminophenyldimethylpyrazolonemercury, etc., has been examined. The aliphatic compounds do not differ very much in their action, but the benzene and pyrazolone compounds show many differences in toxicity and in the relation of the curative to the toxic dose. Sulphamino-compounds show a great lowering of the poisonous nature of mercury preparations without a diminution in their spirillocidal properties, and sulphaminophenyldimethylpyrazolonemercury is especially to be recommended. J. C. W.

Action of Mercury Preparations on Spirochaete Diseases. II. The Toxicology and Pharmacology of Some Mercury Compounds. J. ABELIN (*Chem. Zentr.*, 1912, ii, 1575; from *Deut. med. Woch.*, 1912, **38**, 1822—1825. Compare preceding abstract).—The poisonous nature of mercury compounds is influenced by their

chemical constitution; the introduction of sulpho- or amino-groups or of doubly-linked carbon atoms diminishes their toxicity. The most poisonous compounds are those in which the mercury is easily ionised, such as mercuric chloride. After injection of mercury preparations, the metal is always found in the liver. J. C. W.

The Sugar of the Blood and Urine under the Influence of Continuous Adrenaline Infusion. M. J. Gramenitzki (*Biochem. Zeitsch.*, 1912, 46, 186—209).—Adrenaline was continuously administered to rabbits by Straub's infusion apparatus, and the effect on the sugar content in the blood and urine with varying dilutions of the drug was ascertained. It was found that there is in general a proportionality between the strength of the adrenaline stimulus, and both the resulting hyperglycæmia and glycosuria. Under urethane narcosis, the amount of adrenaline necessary to produce glycosuria is below the normal. Under these conditions, the strength of the adrenaline stimulus necessary to produce glycosuria is less than that required to raise the blood-pressure. The adrenaline administration increases the diuresis within a few minutes, and this effect is often, but not always, accompanied by glycosuria. The diuretic effect of urethane is to be ascribed to its urea components, whereas its glycosuric effects can only be partly ascribed to these.

Under urethane narcosis, artificially introduced sugar disappears more slowly than in normal animals; it also disappears more slowly from bound animals than from animals which are free. Venesection causes a distinct but slight hyperglycæmia, which is sometimes accompanied by glycosuria. The effects of the narcotic, etc., were investigated in some detail in view of criticisms on Ritzmann's work, which was also carried out in Straub's laboratory. In experiments on non-narcotised animals, it was found that the proportionality between the adrenaline stimulus and the effects was more marked than in the narcotised animals. The primary effect is hyperglycæmia, which can be quite marked (up to 0·2%) even when there is no glycosuria. The smallest stimulus necessary to produce glycosuria is higher in non-narcotised than in narcotised animals. The diuretic action of adrenaline follows definite laws, and is independent of the glycosuric effect. The general theory of the drug action is discussed. S. B. S.

Effect of Adrenaline on the Pulmonary Circulation. E. M. Tribe (*Proc. physiol. Soc.*, 1912, xx—xxii; *J. Physiol.*, 45).—The conflicting results of previous workers on this question are probably due to the use of different preparations. Adrenaline preparations free from preservative cause constrictions at body temperatures. Preparations of adrenaline chloride preserved with 0·5% chloretone cause distinct dilatation of the pulmonary vessels. The constriction obtained with pure adrenaline is, however, hardly comparable with that seen in organs supplied by vaso-motor nerves, and the question of the existence of such nerves in the lung-vessels is left undecided.

W. D. H.

The Vascularity of the Liver. VIII. The Influence of Adrenaline on the Arterial Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, 5, 309—324).—The complex nature of the blood supply of the liver renders the interpretation of records a matter of difficulty, and much of this and the following papers is devoted to a discussion of this question. There appears, however, no doubt that adrenaline constricts the arterioles of the liver, and leads then to a rise of pressure in the hepatic artery and an increase in the arterial inflow, the general blood-pressure being also raised. This is followed by a period of lessened inflow, although the hepatic pressure is still high, but the general pressure is only slightly elevated. Exceptions to this rule are explained by the fact that an injection of adrenaline does not necessarily imply that it enters the hepatic artery; it might be swept past the orifice of the artery; a similar accident in the case of arteries supplying other organs might explain unexpected results there. W. D. H.

The Vascularity of the Liver. IX. Influence of Amyl Nitrite on the Arterial Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, 5, 325—328).—Inhalation of amyl nitrite causes a fall of general arterial pressure, but also causes a local change in the liver circulation. The fall of pressure in the hepatic artery is proportional to the general fall. On discontinuing the inhalation the pressure returns very slowly to normal. The arterial inflow is directly proportional to the systemic pressure, and the local changes are attributed wholly to the general effect. W. D. H.

The Vascularity of the Liver. X. The Influence of Adrenaline on the Venous Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, 5, 329—342).—Evidence is adduced that the liver possesses two separate motor mechanisms, one in the terminals of the hepatic artery, and the other in the radicles of the portal vein, both of which are stimulated by adrenaline. W. D. H.

Metabolism Experiments in the Administration of Atophan. WITOLD SKÓRCZEWSKI and J. SOHN (*Chem. Zentr.*, 1912, ii, 1381; from *Zeitsch. expt. Path. Ther.*, 1912, 11, 254—263).—Experiments on normal persons and on sufferers from gout show that the administration of atophan causes an increase in the output of uric acid, which, however, falls off with subsequent doses, more purine bases being discharged. An alteration in the functions of the kidneys is presumed, for a retention of chlorides immediately follows the administration. The atophan urine always gives the diazo-reaction, which becomes weaker after several doses; it also gives the phenol reaction with bromine water, a dirty rose-coloured precipitate with Millon's reagent, a yellow precipitate with phosphotungstic acid, and a green colour with a mixture of ammonium sulphate and ammonia.
J. C. W.

Why Does Atophan Increase the Excretion of Uric Acid? WITOLD SKÓRCZEWSKI (*Chem. Zentr.*, 1912, ii, 1679; from *Zeitsch. expt. Path. Ther.*, 1912, 11, 501—507. Compare preceding abstract).—

The action of atophan is presumed to be an oxidation disturbance, of which the interference in the degradation of uric acid is a special case. This affords an explanation of the variations in uric acid values, the increase in neutral sulphur, and the appearance of the diazo-reaction in atophan urine. J. C. W.

The Formation of Phenol from *p*-Cresol in the Organism of the Dog. MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1912, **46**, 210—224).—In view of Baumann's conceptions as to the degradation of tyrosine in the organism through *p*-cresol and *p*-hydroxybenzoic acid to phenol, the effect of the administration of *p*-cresol was investigated, and it was found to yield phenol; 32—48% of the phenolic substances administered were recovered in the urine, of which 23—46% was in the form of phenol. Various modifications in the technique of phenol and cresol estimation are given, chiefly with regard to the method of bromination, and the addition of sufficient alkali before evaporating the urine to prevent loss of phenol.

S. B. S.

Formation of Glycine in the Body. II. ALBERT A. EPSTEIN and SAMUEL BOOKMAN (*J. Biol. Chem.*, 1912, **13**, 117—132).—Free leucine does not yield glycine, although it undergoes decomposition in the body. When benzoyl-leucine is given with benzoic acid, the output of hippuric acid is much greater than the leucine alone allows. Phosphorus poisoning causes no increased production of glycine or hippuric acid. Phosphorus plus benzoic acid has also no such effect unless the animal is fasting; then the increase must be due to massive disintegration of protein. Much of the glycine liberated on feeding with benzoic acid must be the result of a synthesis in the body. W. D. H.

Tolerance to Nicotine. WALTER E. DIXON and W. E. LEE (*Quart. J. expt. Physiol.*, 1912, **5**, 373—382).—A person tolerant to nicotine may be so because nicotine is not absorbed, but this is unlikely. A second explanation may be that it is more readily destroyed by the tissues. The present experiments were made on rabbits, and in thirteen out of sixteen experiments, tolerance was established, the drug being injected under the skin, or into the blood-stream. The analyses of the tissues show that the second explanation given above is correct, but that all the cells of the body do not possess the power of destroying nicotine in equal measure: the liver is the most effective. Evidence is adduced that the destruction is probably oxidative and due to the action of an enzyme. W. D. H.

The Oxidation of *p*-Phenylenediamine by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, **46**, 317—342).—It is shown in investigations of the oxidative functions of tissues that the *p*-phenylenediamine reaction is better than the indophenol reaction. All tissues can oxidise this substance. The amount of oxygen consumed was in most cases measured, and it was found that in the accessory respiration of the tissues the amount consumed

was the sum of that used up by the tissues, when without the reagent plus the amount necessary to oxidise the reagent. In the primary respiration, on the other hand, the *p*-phenylenediamine oxidation partly replaced the tissue respiration. The oxidation is most intensive in the heart, red muscles, liver and kidney, and much less in the pancreas, spleen, and lungs. With the exception of the pancreas, the tissues maintain their oxidative capacity for a long time after death. Under similar conditions of experiment, most tissues use up the same amount of oxygen for oxidising *p*-phenylenediamine as they do for succinic acid; the brain, however, uses up more. In muscles and liver, no more oxygen is used up if both substances are present than if they are present alone. The blood is an energetic oxidiser, but not the serum, and the action appears to be due mostly to the hæmoglobin, as in the blood of some animals, the oxidative capacity remains after heating to 60°, or treatment with pancreatin. This is not even lost after heating the blood with mineral acids. An aqueous extract of liver inhibits the oxidative capacity of the blood, and the inhibitory action is not destroyed by warming to 60°. Blood has no appreciable oxidative action on succinic acid. S. B. S.

The Influence of Various Factors on the Oxidation of *p*-Phenylenediamine by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, **46**, 343—366).—Small amounts of acid or alkali inhibit oxidation. There is no marked optimal temperature of reaction between 30° and 50°, but the action is lost by heating tissues to 60° for ten minutes. In medium concentrations, salts accelerate the reaction, exerting an inhibitory action at higher concentrations. Up to a certain limit the rate of oxidation increases with an increase of the concentration of the *p*-phenylenediamine. The oxydase is not washed out from the tissues by water, and the washed tissues still contain the oxydase. In oxygen, the reaction is more energetic than in air. The oxydase is destroyed by treating the tissues with alcohol or acetone, or with weak solutions of mineral acids. Aqueous extracts of tissues oxidise in presence of hydrogen peroxide, and this function is not lost on heating. The washed residue of muscular tissue will not oxidise in the presence of the peroxide after heating to 60°. Treatment of tissue with pancreatin diminishes the oxidative capacity. Both fresh and heated pancreatin increase the oxidative capacity of the vegetable polyphenoloxydases. Catalysts accelerating the oxidation of *p*-phenylenediamine and succinic acid are distinguishable from other oxydases by the facts that they are not dissolved out by water, and are destroyed by alcohol, acetone, or trypsin. With the exception of those of the brain, the catalysts appear to be identical. S. B. S.

Pharmacology of Picrotoxin, Picrotin, and Picrotoxinin. ALFREDO CHISTONI (*Chem. Zentr.*, 1912, ii, 371—372; from *Arch. Farmacol. sperim.*, 1912, **13**, 220—240).—Picrotoxin and picrotoxinin, in concentration 1 in 2000, reduce the tone and the amplitude of the contractions of smooth muscle, but in concentration 1 in 10,000 they increase the amplitude and diminish the number of contractions,

and either do not influence or slightly increase the tone of smooth muscle; picrotin is inactive.

All three substances, in a concentration of 1 in 2000, slightly increase the tone of striped muscle.

The frequency and contraction of the amphibian heart are affected by picrotoxin and picrotoxinin, due to their action on the muscle; picrotin is inactive.

Picrotoxin and picrotoxinin intravenously injected in dogs reduce the pulse and increase the blood pressure, due to stimulation of the pneumogastric and the vasomotor centres.

All three substances (1 in 2000—4000) still the isolated hearts of cats and rabbits, but this effect ceases when the poisons are removed. In a concentration of 1 in 80,000, picrotoxin at first quickens and then slows the heart's action, and these effects are not inhibited by the previous application of atropine. Picrotoxinin (1 in 80,000) at first strengthens and quickens the heart's action by its effect on the vagus, but finally stills the heart by direct action on the muscle fibres. Picrotin (1 in 40,000) accelerates the heart-beats and reduces the strength of the pulse.

T. A. H.

The Poisonous Nature of Methyl and Ethyl Alcohols. ALEXANDER LANGGAARD (*Chem. Zentr.*, 1912, ii, 1382—1383; from *Berl. klin. Woch.*, 1912, **49**, 1704).—Methyl alcohol is more poisonous than ethyl alcohol when taken in repeated small quantities, but ethyl alcohol is much more dangerous when taken in a single large dose.

J. C. W.

Hæmolytic Substances obtained from Serum, and the Vitellus of Egg, Submitted to the Action of Venoms. C. DELEZENNE and (Mlle.) S. LEDEBT (*Compt. rend.*, 1912, **155**, 1101—1103. Compare *ibid.*, 1911, **152**, 790; **153**, 81).—Cobra venom acts on the serum of horse blood or the vitellus of egg, giving rise, by diastatic action of the venom on the lecithin, to *haemolysin*, which differs from lecithin in that it is soluble in water and insoluble in ether, and its molecule does not contain any unsaturated fatty acids (oleic acids). It resembles lecithin in its solubility in alcohol.

In the case of the serum the venom-serum mixture attains a maximum hæmolytic power, which then decreases until the mixture is inactive. At the same time a very fine precipitate of calcium soaps (palmitate and stearate) is produced. This diminution in activity, which is peculiar to serum, corresponds with further decomposition of the hæmolysin, and if the serum is dialysed prior to addition of the venom, the second stage in the action does not occur, and it behaves in the same manner as the vitellus of egg. The liquid resulting from the dialysis of the serum produces this secondary effect on addition to a venom-vitellus mixture.

W. G.

Chemistry of Vegetable Physiology and Agriculture.

A Hygienic Pipette for Bacteriological and Chemical Work. SERGEI TSCHACHOTIN (*Centr. Bakt. Par.*, 1912, i, 67, 319—320).—The pipette is intended to facilitate the removal of liquid cultures of pathogenic organisms, volatile poisonous compounds, or liquids above flocculent precipitates. A double-bored rubber cork is cut transversely, and between the two parts an ordinary rubber cap, such as is used for closing bacterial tube-cultures, is interposed and the three cemented together. Holes are made through the rubber cap with a hot needle, and two tubes are introduced: (*a*) a short straight one projecting slightly above and below the cork; (*b*) a siphon tube having the longer arm through the cork. A test-tube, having a diameter slightly larger than that of the rubber cork, is used as receiver, and closed by means of the flange of the rubber cap. The short arm may then be placed in the liquid to be pipetted off, and the cork of the pipette depressed slightly into the tube; the short glass tube is then closed by the fore-finger and the cork raised slightly. By this means a sufficient vacuum is created in the tube to cause the liquid to siphon over, and the flow is stopped by raising the short arm out of the liquid.

H. B. H.

Detection of Chitin in Bacteria. A. VIEHOEVER (*Ber. Deut. botan. Ges.*, 1912, 30, 443—452).—Chitin was found to be present in a number of bacteria, and the occurrence of glucosamine in bacterial material is attributed chiefly to the abundant presence of chitin rather than to glucoproteins.

The results are of interest in removing a supposed difference between fungi and bacteria. That fungi contains chitin has been known for a long time.

N. H. J. M.

Gas Metabolism of Bacteria. I. Fermentation of Dextrose by Bacillus coli, B. typhosus, and Bacterium welchii. FREDERICK G. KEYES and LOUIS J. GILLESPIE (*J. Biol. Chem.*, 1912, 13, 291—304).—The evolution of gas accompanying bacterial growth on media containing dextrose was studied by an exact method. Dextrose peptone media yield with *B. coli* more carbon dioxide than hydrogen on anaërobic fermentation; on a medium of ammonium lactate, di-sodium phosphate, and dextrose, nearly equal volumes of the two gases are obtained, the mean value of $CO_2:H_2$ being 1·06. This ratio is raised by the presence of oxygen, and by increase of phosphate. With *B. typhosus* the ratio is never below 19; with *Bacterium welchii* it is 1·48.

W. D. H.

Gas Metabolism of Bacteria. II. The Absorption of Oxygen by Growing Cultures of Bacillus coli and Bacterium welchii. FREDERICK G. KEYES and LOUIS J. GILLESPIE (*J. Biol. Chem.*, 1912, 13, 305—310).—For both micro-organisms the absorption of oxygen

simulates a unimolecular reaction, but the respiratory quotients are widely different. With varying oxygen pressures the ratio $CO_2 : H_2$, varies enormously for *B. coli*, but only slightly for *Bact. welchii*.

W. D. H.

Activation of Certain Processes of Microbic Oxidation by Uranium Salts. HENRI AGULHON and R. SAZERAC (*Compt. rend.*, 1912, 155, 1186—1188).—A further study of the influence of uranyl acetate on *Mycoderma aceti* (compare A., 1912, ii, 973) and a comparative trial of the influence of uranyl nitrate and uranyl acetate on the sorbose bacteria. In the case of the acetic acid ferment, 1 part of uranyl acetate per 1000 gives an increase of 57% in the acid production, and even at a dilution of 1 in 100,000 an increase is shown at the end of seven days. With the sorbose bacteria, uranyl nitrate increases the rate of oxidation up to concentrations of 1 in 5000, but stops all fermentation at 1 in 1000. At all concentrations the acetate has a more favourable influence than the nitrate, and 1 part of the acetate in 10,000 produces an increase yield of 76%.

W. G.

Action of Infinitesimal Doses of Different Alkaline Substances, Fixed or Volatile, on the Vitality of Microbes. AUGUSTE TRILLAT and M. FOUASSIER (*Compt. rend.*, 1912, 155, 1184—1186).—A study of the effect of adding minute quantities of various alkalis and organic bases to distilled water, to which is then added a drop of dilute, microbic, aqueous emulsion, containing no nutrient medium. The results, expressed in numbers of colonies formed, are given for the organism *M. prodigiosus*. With pure water there is slight growth for twenty-four hours and then the organism dies. Death is immediate with sodium hydroxide until a dilution of 1 in 50,000 is reached, and it is only in the case of ammonia, at dilutions of 1 in 50,000 and higher, that there is any marked increase in the number of colonies. With organic bases at higher orders of dilution (1 in 250,000) the number of colonies formed is greater with fatty amines than ammonia, and still greater with aromatic amines, although even here death ensues after fifteen days. The addition of traces of putrefactive gases to the distilled water allows cultivation to proceed even after three months.

W. G.

Putrefaction with Special Reference to the Proteus Group. LEO F. RETTGER and CLYDE R. NEWELL (*J. Biol. Chem.*, 1912, 13, 341—346).—Putrefaction is taken to mean decomposition of protein with the production of malodorous substances. The power to bring this about has been attributed to various members of the *Proteus* group acting anaërobically. The present experiments do not confirm this.

W. D. H.

The Influence of Organic Acids on the Fermentation by Yeast. FRITZ JOHANESSOHN (*Biochem. Zeitsch.*, 1912, 47, 97—117).—Formic acid and its higher homologues accelerate, in sufficiently dilute solutions, the rate of fermentation by yeast. The optimal action for each acid lies at the same molecular concentration. The smallest

quantities of the acids which stop fermentation do not kill the yeast. The stoppage of fermentation depends on the concentration of the acid and not on the absolute quantity present. The relationship between this concentration and the quantity of yeast is not a simple proportional one, but can be represented by the equation of a parabola. No appreciable adsorption of acids by yeast takes place. The essential action of acids is to be ascribed, not to the ions, but to the whole undissociated molecule. S. B. S.

The Mechanism of Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Biochem. Zeitsch.*, 1912, **46**, 483—489).—A reply to the criticisms of Harden and Young (A., 1912, ii, 670). S. B. S.

The Mechanism of Alcoholic Fermentation. II. ALEXANDER VON LEBEDEV and N. GRIAZNOV (*Ber.*, 1912, **45**, 3256—3272. Compare A., 1911, ii, 816, 1122).—Pure glyceraldehyde is fermented by extract of dried yeast directly to carbon dioxide and alcohol. Hexosephosphoric ester is not formed as intermediate compound as in the case of the fermentation of dihydroxyacetone.

It is further shown that during the fermentation of sugar by yeast extract, acetaldehyde is not reduced to alcohol; on the other hand, in the absence of sugar, yeast extract is able to reduce acetaldehyde to alcohol. This reduction is effected by an enzymatic process.

It is considered that during fermentation hexose is hydrolysed to two trioses, one of which, glyceraldehyde, loses hydrogen, forming pyruvic acid, which undergoes rearrangement immediately and breaks down into acetaldehyde and carbon dioxide (compare Neuberg, A., 1911, ii, 976, 1019, 1020). Methylglyoxal hydrate is possibly an intermediate product (Neuberg and Kerb, A., 1912, ii, 973); preliminary experiments indicate that methylglyoxal is fermentable by yeast juice.

The decomposition of hexose into two molecules of triose is regarded as a reversible reaction; it will proceed when part of the triose is withdrawn as hexosephosphate, so that this last compound acts as a regulating factor. The following complete scheme is suggested for fermentation:

$$4C_6H_{12}O_6 = 8C_3H_6O_3.$$

Glyceraldehyde.	Dihydroxyacetone.
$4C_3H_6O_3 - 4H_2 = 4C_3H_4O_3$	$4C_3H_6O_3 + 4RHPO_4 =$
$4C_3H_4O_3 = 4C_2H_4O + 4CO_2$	$4C_3H_5O_2RPO_4 + 4H_2O$
$4C_2H_4O + 4H_2 = 4C_2H_5{\cdot}OH$	$= 2C_6H_{10}O_4(RPO_4)_2 + 4H_2O$
	$= 2C_6H_{12}O_6 + 4RHPO_4$

$$2C_6H_{12}O_6 = 4C_3H_6O_3, \text{ etc.}$$

E. F. A.

Influence of Pressure on Alcoholic Fermentation. LÉON LINDET and L. AMMANN (*Bull. Soc. chim.*, 1912, [iv], **11**, 953—956).—Regnard has shown already that under a pressure of 600 atmospheres yeast still ferments sugar solutions. In the present paper it is demonstrated that under such pressures as may occur in practice in fermenting liquids with yeast in closed vessels, the reproduction of

yeast and the fermentation go on at the same rate as under atmospheric pressure, although when the experiments are conducted under such conditions that the air is not renewed, fermentation and the multiplication of the yeast-cells take place more slowly, although the same production of carbon dioxide and alcohol is eventually reached.

T. A. H.

Is Ethyl Alcohol Produced by Yeast Fermentation in Absence of Sugar? CARL NEUBERG and JOHANNES KERB (*Chem. Zentr.*, 1912, ii, 1299—1300; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 114—120).—Since pyruvic acid is easily attacked by yeast with the formation of acetaldehyde (A., 1911, ii, 1019) it was expected that the ferment alone might be able to carry the reduction further. No alcohol could be found, however, but in the presence of sugar, much less aldehyde was formed than the amount of pyruvic acid destroyed would warrant. It seemed, therefore, that in normal alcoholic fermentation, a substance is produced which can reduce pyruvic acid or acetaldehyde to alcohol. Formic acid suggested itself, but was found to be without influence. Glycerol, however, had the effect of largely diminishing the output of acetaldehyde. J. C. W.

The Primary Transformation of Hexoses by Alcoholic Fermentation. HANS VON EULER and TH. BERGGREN (*Chem. Zentr.*, 1912, ii, 1383—1384; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 203—218).—The addition of yeast extract to living yeast expedites fermentation by 100%, and the difference, ΔC, between the change in optical rotatory power and the carbon dioxide developed (compare A., 1912, ii, 377) is increased by 20%. Assuming that fermentation proceeds in two stages, hexose $\longrightarrow$ intermediate product and intermediate product $\longrightarrow$ alcohol and carbon dioxide, it follows that, if the extract contains only one co-enzyme the first stage will be accelerated, but if there is a co-enzyme in the extract appropriate to each stage, then the two reactions will be unequally accelerated according to the relative amounts of the co-enzymes. Sodium nucleate also increases the activity of living yeast. J. C. W.

The Effect of Phosphates on the Work of the Proteolytic Enzymes in Yeast. NICOLAUS IWANOV (*Chem. Zentr.*, 1912, ii, 1384—1385; from *Zeitsch. Garüngsphysiol. Mykologie*, 1912, 1, 230—252).—The action of antiproteolytic by-products in yeast fermentation may be overcome by the addition of acid phosphates. Experiments with dead yeast cells (hefanol) show that the decomposition of albumin increases with the concentration of potassium dihydrogen phosphate, and that this increase is independent of temperature. By decreasing the volume of liquid, or by the addition of autolysis products, the action is still further increased, whereas leucine and tyrosine do not influence the process, but dipotassium hydrogen phosphate hinders it.

The proteolytic enzyme may be partly extracted from hefanol by means of water. When heated to 80°, it becomes inactive, but the addition of potassium dihydrogen phosphate revives its activity. It

seems that this salt is able to regenerate the peptase and to promote its action. J. C. W.

Comparative Influence of Potassium, Rubidium, and Cæsium on the Development and Sporulation of Aspergillus niger. BENJAMIN SAUTON (*Compt. rend.*, 1912, 155, 1181—1183).—*Aspergillus niger* was cultivated on Raulin's liquid in the presence of equivalent amounts of potassium, rubidium, and cæsium as chlorides, and the crops weighed after four days at 37°. Potassium causes an enormous increase in the crop, which is diminished by 50% on replacing the potassium by rubidium, whilst cæsium is not a nutrient substance for the organism. In a mixture of the chlorides, *Aspergillus niger* fixes the potassium before the rubidium and cæsium, thus forming a means of freeing the two latter from the last traces of the former metal. Potassium plays an important part in the sporulation, although in the absence of zinc this could not be conclusively demonstrated. On substituting rubidium or cæsium for potassium no spores are formed. W. G.

The Scission of α- and β-Methylglucoside by Aspergillus niger. ARTHUR W. DOX and RAY E. NEIDIG (*Biochem. Zeitsch.*, 1912, 46, 397—402).—*Aspergillus niger* acts on the two glucosides in exactly the opposite way to that in which yeast acts, for it readily hydrolyses the β-form (100% within six days), whereas it acts only slowly on the α-form, hydrolysing only 8% in twenty days. No capacity of adaptation of the ferment to the α-form could be demonstrated. S. B. S.

The Behaviour of Moulds (Aspergillus niger and Penicillium crustaceum) towards Phytin. M. A. JEGOROV (*Zeitsch. physiol. Chem.*, 1912, 82, 231—242).—The moulds mentioned grow well in a solution of phytin, and assimilate its phosphorus, especially in the presence of sucrose and peptone or glycerol. They split off phosphoric acid in high measure from the phytin. W. D. H.

Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds. ALEXANDER KOSSOWICZ (*Bied. Zentr.*, 1912, 41, 791—792; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 60—60).—Pure cultures of the following moulds were found to assimilate urea, uric acid, hippuric acid, and glycine under sterilised conditions: *Botrytis bassiani*, *Aspergillus niger*, *Isaria farinosa*, a *Fusisporium*, *Mucor Boidin*, and *Phytophthora infestans*. *Penicillium brevicaule* and *P. crustaceum* utilise urea, uric acid, and glycine, whilst *Cladosporium herbarum* and *Aspergillus glaucus* only utilised urea and uric acid as sources of nitrogen. N. H. J. M.

The Apparent Respiration of Dead Cells in the Reduction of Pigments. OTTO MEYERHOF (*Pflüger's Archiv*, 1912, 149, 250—274).—Neutral and weakly alkaline acetone yeast possesses a measurable power of taking up oxygen, and this is increased in the presence of methylene-blue. In the presence of dead cells, reduction

of methylene-blue occurs also, but it occurs also if the dead cells are absent. It is, therefore, not due to anything of the nature of vitality. In one living animal cell, the egg of the sea-urchin, dissolved oxygen is present. W. D. H.

The Action of Uranium on the Plant Cell. C. ACQUA (*Chem. Zentr.*, 1912, ii, 1471; from *Arch. Farmacol. sperim.*, 1912, 14, 81—84).—Dilute solutions of uranium salts (1 : 20,000 to 1 : 40,000) are absorbed by the cells of the roots of higher plants, where they hinder the division of the nuclei, and, consequently, the growth. The cells of the green parts are less permeable to uranium salts, and are therefore scarcely injured. Thorium and manganese salts have a similar but much smaller effect. J. C. W.

Absorption of Aniline Dyes in Living Plant Cells. E. KÜSTER (*Bied. Zentr.*, 1912, 41, 763—764; from *Jahrb. wiss. Bot.*, 1911, 50, 261).—It is shown that a considerable number of dyes, insoluble in fats, are abundantly taken up by plant cells. Overton's lipoid hypothesis regarding the nature of the outer layer of protoplasm is, therefore, insufficient, whilst Ruhland's opinion that there is no relation between the diffusibility of dyes and their penetration into plant cells is incorrect. N. H. J. M.

The Physical Character of Bio-electrical Differences of Potential. REINHARD BEUTNER (*Biochem. Zeitsch.*, 1912, 47, 73—93). —The difference of potential at the contact surfaces—part of plant/aqueous solution of an electrolyte—can be altered in the sense that increasing dilution of the electrolyte makes the solution more positive. The change can be expressed by the following equation:

$$\text{Pot. diff. } 1 - \text{Pot. diff. } 2 = 58 \log \frac{c_1}{c_2} - 58 \log \frac{1 + \sqrt{1 + 10^6 m^2 c_1^2}}{1 + \sqrt{1 + 10^6 m^2 c_2^2}}$$

where

$$\log \frac{1}{m} = \frac{\text{Limiting value of potential difference} - \text{Pot. diff. for } c = n/500}{58}.$$

The method of arriving at these equations is given, and also an experimental verification of the same. The biological significance is also discussed. S. B. S.

Sterile Cultures of a Higher Plant. Assimilation of Nitrogen as Ammonia and as Nitrates. IVAN SCHULOV (*J. exper. Landw.*, 1912, 13, 200—205 (in Russian), 205—206 (German Abstr.). Compare Hutchinson and Miller, A., 1909, ii, 923).—The results of sand culture experiments, under sterilised conditions, showed that nitrogen in the form of ammonium sulphate is assimilated by maize plants. It is also shown that the availability of phosphorite is considerably increased by the employment of ammonium nitrate, and that ammonium nitrate overcomes the injurious action of ammonium sulphate.

N. H. J. M.

Localisation and Function of Potassium in Plants. TH. WEEVERS (*Bied. Zentr.*, 1912, 41, 764—765; from *Rec. trav. bot. Néerland.*, 1911, 8, 289—332).—By means of Macallum's reagent

(sodium cobaltinitrate with ammonium sulphide and glycerol) it was found that potassium is present in all parts of *Thallophytes*, whilst negative results were obtained with the pollen grains of crocus and tulips. The greatest amount of potassium in *Phanerogams* was found in the young, embryonal tissues rich in plasma, and in the parenchyma of leaves, seeds, roots, and stems.

The conclusion is drawn that potassium takes part in the production of proteins. Its absence in the chlorophyll is opposed to the theory of Grafe and Stoklasa, that it takes part in the process of assimilation. N. H. J. M.

Chlorogenic and Saccharic Acids in Latex. K. Gorter (*Rec. trav. chim.*, 1912, **31**, 281—286).—The colour reactions with ferric chloride which de Jong and Tromp de Haas (A., 1904, ii, 762) have shown to be characteristic of the latex of certain plants resemble the reactions with the chlorogenic acid obtained from coffee (A., 1908, i, 186). A delicate test for this acid is now described. It consists in boiling the suspected substance with dilute hydrochloric acid for an hour, extracting with ether, and shaking the washed and not too concentrated extract with very dilute ferric chloride, when a violet coloration is produced. By this means it is shown that chlorogenic acid is present in the latex of *Ficus elastica* and of *Castilloa elastica*. It has actually been isolated from the latter substance, 300 grams of the latex yielding 0·3 gram chlorogenic acid, m. p. 208°, $[\alpha]_D^{26}$ −35·2°. The latex of *Ficus elastica* contains, in addition, an organic magnesium salt, which has now been isolated and given the formula

$$C_6H_8O_8Mg,3H_2O.$$

The free acid has $[\alpha]_D^{26}$ + 36·5°, and gives a sparingly soluble potassium salt, which closely resembles potassium disaccharate, and a diphenylhydrazone, m. p. 210°, which is identical with that derived from *d*-saccharic acid. This magnesium salt is the first indication of the occurrence of *d*-saccharic acid in nature. J. C. W.

The Carboxylase of Higher Plants. W. Zaleski and Elisabeth Marx (*Biochem. Zeitsch.*, 1912, **47**, 184—185).—Neuberg has shown that yeast can ferment pyruvic acid with evolution of carbon dioxide. The authors now show that the addition of this acid to powdered pea-seeds causes an increase of the post-mortal production of carbon dioxide, which takes place with equal energy in air and hydrogen. S. B. S.

Basic Constituents of Fly Agaric. E. Buschmann (*Chem. Zentr.*, 1912, ii, 613; from *Pharm. Post*, 1912, **45**, 453—454).—A methyl alcohol extract of fly agaric (*Amanita muscaria*) by precipitation with phosphotungstic acid and silver nitrate yielded hypoxanthine and xanthine, the former predominating (compare Zellner, *Chemie der höheren Pilze*, 1907). T. A. H.

The Inulin Metabolism of Cichorium Intybus (Chicory). II. The Formation and Storage of Inulin. Viktor Grafe and V. Vouk (*Biochem. Zeitsch.*, 1912, **47**, 320—330. Compare A., 1912, ii, 977).—From estimations of reducing sugar and inulin in different

parts of the plant collected at different periods, the following conclusions were drawn. The inulin is not merely a reserve material, but is intimately connected with the general carbohydrate metabolism, as it can be readily detected macrochemically in the parenchymatous cells of the leaves of young plants. No difference in the inulin and lævulose content of leaves of plants collected in the morning and afternoon could be detected. From this fact the conclusion is drawn that new carbohydrate is formed during the day in such quantity that an equilibrium is maintained between the lævulose and inulin. As the development of the root progresses there is a constant increase in the inulin content, accompanied at first by a diminution of the lævulose; the latter increases in quantity again as the roots ripen.

S. B. S.

The Organic Phosphoric Acid of Cotton-seed Meal. R. J. ANDERSON (*J. Biol. Chem.*, 1912, **13**, 311—324).—The organic phosphorised substance from cotton-seed meal is probably either phytin or an isomeride; this is to be ascertained by further work.

W. D. H.

Pigments of the Fucoideæ. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1912, **82**, 221—230).—The fucoideæ contain carrotene and a crystalline, yellow pigment probably identical with xanthophyll. They further contain a yellow pigment, phycoxanthin, which differs from xanthophyll in being soluble in light petroleum. E. F. A.

Presence of Gentiopicrin, Gentianose, and Sucrose in the Fresh Roots of Gentiana Asclepiadea. MARC BRIDEL (*Compt. rend.*, 1912, **155**, 1164—1166).—The author has isolated and characterised gentiopicrin, gentianose, and sucrose from the fresh roots of *Gentiana Asclepiadea*, and has obtained indications of the presence of another carbohydrate, hydrolysable by invertin. W. G.

The Constituents of Ipé tabaco Wood (Bignonia tecoma). OTTO A. OESTERLE (*Chem. Zentr.*, 1912, ii, 1666—1667; from *Schweiz. Woch. Chem. Pharm.*, 1912, **50**, 529—532).—In order to investigate the nature of Lee's tecomin (T., 1901, **79**, 284), the alcoholic extract of *B. tecoma* wood has been freed from resinous matter by means of benzene and light petroleum, leaving a mixture which was partly soluble in boiling sodium carbonate solution. The soluble substance crystallised in yellow needles or leaflets, m. p. 142—143°, soluble in alkalis and alkali carbonates with intense red colours which disappeared on reduction, but soon reappeared in the air. Tecomin is possibly identical with lapachol. From the substance which remained undissolved by sodium carbonate, light yellow needles, m. p. 242°, were obtained. J. C. W.

Variations of the Fatty Matters, Sugars, and Saponin during the Maturation of Seeds of Lychnis Githago. (Mlle.) MARIE KORSAKOV (*Compt. rend.*, 1912, **155**, 1162—1164).—The fatty matters, sugars, and saponin have been estimated in the seeds of *Lychnis Githago*

at three stages in their development: (*a*) just after flowering, when young and white; (*b*) further advanced but still white; (*c*) almost ripe and black. The results show a marked decrease in the content of fatty matters and sugars, reducing and non-reducing, and an increase in the saponin content with advance in development. The young seeds only contain traces of saponin, and the amount of saponin in the other organs of the plant being practically nil, it seems that the glucoside must be formed in the seed itself. W. G.

Presence of Gentiopicrin in Swertia perennis. MARC BRIDEL (*Compt. rend.*, 1912, **155**, 1029—1031; *J. Pharm. Chim.*, 1912, [vii], **6**, 481—484).—*Swertia perennis* contains the glucoside gentiopicrin, which can be isolated in the pure state and hydrolysed by emulsin (compare Bourquelot and Bridel, A., 1910, ii, 234). There are also indications of the presence of a carbohydrate, which is only very slowly hydrolysed by emulsin. W. G.

Occurrence of Trehalose, Vanillin, and *d*-Sorbitol. EDMUND O. VON LIPPMANN (*Ber.*, 1912, **45**, 3431—3434).—After exposure to a sudden sharp frost in July, the flowers of some blooming rushes, *Carex brunescens*, growing in a sheltered spot, were observed to be covered with minute, hard, white crusts, which proved to be hydrated trehalose, $C_{12}H_{24}O_{11},2H_2O$.

The flowers of an orchid, *Gymnadenia albida*, growing last summer on the heights above Davos, were observed by the author to have a strong odour of vanilla; vanillin was isolated from them. Under normal conditions of growth, the flowers of this orchid contain little or no vanillin.

During last year's wet summer, many fungi in the fields near Kissingen grew in enormous quantities and to prodigious size, in particular, a variety of *Boletus bovinus*, which reached the dimensions of a dinner plate. After fine weather had set in, a number of the tops of these fungi, which had been struck off by a passer-by and had partly dried, were found to be covered with a network of a crystalline substance which on examination proved to be hydrated *d*-sorbitol. C. S.

Chemical means of Protecting Plants from Frost. N. A. MAXIMOV (*Ber. Deut. bot. Ges.*, 1912, **30**, 504—416. Compare A., 1912, ii, 476).—The supposition that the protective action of the substances employed depends on the eutectic point of the solution is confirmed by the results of further experiments in which mixtures instead of single substances were used. A mixture of mannitol and potassium nitrate considerably increased the power of resisting cold, whilst the two substances, singly, have very little effect.

As regards the connexion between the protective action and the permeability of the plasma for the protective substance, it is now shown that the action takes place immediately, and that the result depends on the action of the solution on the surface of the plasma. From this it follows that the death of plants by freezing is due to injury to the surface of the plasma. N. H. J. M.

Alfalfa. IV. Enzymes Present in Alfalfa Seeds. C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, **34**, 1730—1740).—In continuation of the investigation of alfalfa (*Medicago sativa*) (A., 1912, ii, 80, 239, 976), a study has been made of the enzymes contained in the seeds. The results show that the seeds contain enzymes, which, like amylase and emulsin, are capable of hydrolysing starch and amygdalin respectively; an enzyme which coagulates milk, like rennin; an enzyme, which like the peroxydases, precipitates purpurogallin from a pyrogallol solution containing hydrogen dioxide, and an enzyme, resembling proteases in being able to digest casein and Witte peptone. This protease is found to be a vegetable erepsin, since it will not begin the digestion of egg-albumin, blood-serum, legumin, or conglutin, and its digestion of casein and Witte peptone is checked to some extent by the presence of egg-albumin or blood-serum. The seeds do not appear to contain invertase or lipase. E. G.

Comparative Efficiency for Growth of the Total Nitrogen from Alfalfa Grass and Corn Grain. EDWIN B. HART, GEORGE C. HUMPHREY, and F. B. MORRISON (*J. Biol. Chem.*, 1912, **13**, 133—154).—Experiments on heifers show that the utilisation of nitrogen for growth is as efficient when the source is alfalfa hay as when it is corn kernel. There was no sudden increase or decrease in the nitrogen of urine or fæces when the animals were suddenly changed from one ration to the other. The amide-nitrogen, which is high in the grass, is therefore not valueless. The effect on milk production will be treated later. In growing heifers, the creatinine output rises with increased storage of nitrogen. W. D. H.

Observations on the Action of Fluorine in Nature. UGO ALVISI (*Gazzetta*, 1912, **42**, ii, 450—452).—The author confirms the presence of fluorine in wheat (when ripe) and in human teeth. He suggests the employment of calcium silicofluoride as a manure.

R. V. S.

Reducing Substances Present in Fresh Sugar Beets. Their Influence on the Direct Estimation of Sucrose in the Beet. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 239—253).—Freshly harvested sugar beets always contain a small quantity of reducing sugar, amounting to 0·05—0·27 gram per 100 c.c. of the sap. This amount is independent of the initial richness of the beet in sucrose, and does not vary in different parts of the same beet. The estimation is made in the sap clarified by treatment with neutral lead acetate; basic lead acetate precipitates some of the reducing sugar. Beets of inferior quality contain 2—2·5 grams of reducing sugar per 100 c.c. of sap. Beets stored in silos lose some of their sucrose, but the amount of reducing sugar does not increase. Beets damaged during harvesting or transport contain 0·3—0·35 gram of reducing sugar; in sickly beets the quantity increases to 0·4—0·5 gram per 100 c.c. of sap.

Reducing sugar is not formed during diffusion. The amount arising

during the processes of manufacture is very small when proper care is exercised.

The presence of this reducing sugar renders the polarimetric estimation of the sucrose in the beet-juice inaccurate. E. F. A.

Sesame Cake. ACH. GRÉGOIRE and EM. CARPIAUX (*Bull. Soc. chim. Belg.*, 1912, **26**, 479—485).—A number of samples of sesame cake have been examined with respect to the content of pure ash, lime, fat, acidity of fat, and oxalic acid. The results show great variations in the composition of the commercial products.

The pure ash contains, as a mean value, 34·5% of lime, the extreme values being 28·4% and 39·8% respectively. This determination may be employed for controlling the purity of sesame cake, since the great majority of other seeds yield an ash relatively poor in lime. Sesame cake, free from oil and earth, contains an average of 1·99% anhydrous oxalic acid, the individual determinations varying between 1·44% and 2·96%. This value is not sensibly altered when the oil becomes rancid. Free oxalic acid could not be detected. H. W.

The Black Earths of the Valley of l'oued R'Dom in Morocco. G. GIN (*Compt. rend.*, 1912, **155**, 1166—1167).—An account of a black arable earth from a fertile valley traversed by l'oued R'Dom. A description of the earth and results of chemical analyses are given. It is found to support vegetation even in the warm, dry months, and this is supposed to be due to the presence of a trihydrated aluminium oxide in the clay, which supplies the necessary water during the dry months, and recoups itself at the next wet season. The black colour is due to an amorphous humic substance, which is partly soluble to a brown solution in potassium hydroxide. W. G.

Agronomic Study of Manganese. P. NOTTIN (*Compt. rend.*, 1912, **155**, 1167—1169).—A study of the behaviour of different soils towards soluble manganese salts. Soil has the power of rendering the manganese insoluble and fixing it, the constituents of the soil, however, having different absorbent powers. Silica and humus play no part in the manganese fixation. Chalk produces fixation of the manganese by interchange of the calcium and manganese. Natural clay also has a marked absorbent power, independent of the lime present. W. G.

Nitrolim and its Decomposition in the Soil. III. C. J. MILO (*Chem. Zentr.*, 1912, ii, 1393; from *Med. Proefstat. Java-Suikerind*, 1912, 601—634. Compare A., 1912, i, 16).—Nitrolim is hygroscopic, and absorbs water and carbon dioxide with liberation of nitrogen. The calcium cyanamide decomposes into cyanamide and carbamide, which, with the help of micro-organisms, gives rise to ammonium carbonate. In soils which are only slightly absorptive, the calcium cyanamide gives basic salts and cyanamide, and further decomposition proceeds very slowly. J. C. W.

Organic Chemistry.

Purification of Saturated Hydrocarbons by means of Potassium Permanganate. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1748—1753).—Saturated hydrocarbons, when prepared by the reduction of their halogen derivatives, are usually contaminated with unsaturated hydrocarbons, and the same is the case with trimethylenic hydrocarbons prepared by Gustavson's method. The removal of these impurities is an easy matter when the saturated hydrocarbons are stable to concentrated sulphuric acid or to fuming nitric acid; but in some cases the unsaturated hydrocarbons are converted into saturated ones by these reagents, and in certain others the carbon-atom skeleton undergoes isomerisation.

The author has investigated the efficacy of potassium permanganate as a means of purification in these exceptional instances. The results show that the complete removal of small admixtures of the unsaturated compounds in this way is very difficult, and is accompanied by the loss of much of the saturated hydrocarbons. As the concentration of the unsaturated hydrocarbon in the mixture diminishes, its rate of oxidation decreases, until finally it may become less than that at which the saturated compound oxidises; thus a mixture containing 15 parts of menthane and 5 parts of menthene is converted into one containing 11·5 and 2·5 parts respectively by one oxidation, these amounts becoming 7·2 and 0·8, and 3·7 and 0·3 after successive oxidations. Somewhat similar results are obtained with mixtures of menthane and limonene. T. H. P.

Fractional Distillation of Coal. LÉO VIGNON (*Compt. rend.*, 1912, **155**, 1514—1517).—The author has distilled various samples of coal at successive temperatures of 400°, 600°, 850°, 1000° and 1200°, and analysed the gaseous mixtures evolved at these temperatures. The results show (1) that the unsaturated hydrocarbons (acetylene, ethylene, etc.) almost all pass over below 600° and disappear entirely at higher temperatures; (2) methane and its homologues are very abundant (60—80% of total gas) up to 800°, after which they decrease rapidly with rise in temperature; (3) from 800—1000° hydrogen predominates, but in its turn diminishes above 1000°; (4) very high temperatures favour the formation of carbon monoxide.

Rise in distillation temperature produces an increase in the total volume of gas evolved, but a diminution in its calorific power.

W. G.

A New Method for Determining the Position of the Double Bond. JOH. JEGOROV (*J. pr. Chem.*, 1912, [ii], **86**, 521—539).—The method consists in combining the unsaturated compound with nitrogen peroxide, and heating the resulting additive compound with concentrated hydrochloric acid, whereby the molecule becomes ruptured at the position originally occupied by the double linking with the forma-

tion of two carboxylic acids: $R\cdot CH{:}CHR^1 \longrightarrow NO\cdot O\cdot CHR\cdot CHR^1\cdot NO_2$, or $NO_2\cdot CHR\cdot CHR^1\cdot O\cdot NO \longrightarrow R\cdot CO_2H + R^1\cdot CO_2H$.

The transformation of a nitrite into a carboxylic acid has been investigated in the case of amyl nitrite, which, under the influence of hydrochloric acid, yields amyl alcohol and an ester, presumably amyl valerate, the valeric acid being formed by the oxidising action of the nitrite on the amyl alcohol.

When heated with water at 160—170°, the light yellow, oily, additive compound of oleic acid and nitrogen peroxide yields pelargonic acid, *ω-nitrononane*, azelaic acid, and *θ-nitrononoic acid*. The nitro-compounds could not be isolated in a state of purity, and therefore were identified by reducing them to the corresponding amino-compounds.

θ-Aminononoic acid, $NH_2\cdot CH_2\cdot[CH_2]_7\cdot CO_2H$, was isolated in the form of its *platinichloride* from the above mixture by distillation in steam, and reduction of the residual nitrononoic and azelaic acids with tin and hydrochloric acid.

Nonylamine is a viscid liquid, and forms a *hydrochloride* which becomes black when heated without showing a definite m. p.; the *platinichloride*, $2C_9H_{19}\cdot NH_2,H_2PtCl_6$, crystallises in golden-yellow needles.

When heated with concentrated hydrochloric acid, the additive compound of oleic acid and nitrogen peroxide yields pelargonic and azelaic acids, together with hydroxylamine.

From these results the conclusion is drawn that the additive compound consists of a mixture of two isomerides (I) and (II), which, when heated with water, undergo the transformations shown in the following scheme:

$$\text{(I.) } 2C_8H_{17}\cdot CH(NO_2)\cdot CH(O\cdot NO)\cdot C_7H_{14}\cdot CO_2H \longrightarrow H_2O + N_2O +$$
$$2C_8H_{17}\cdot CH(NO_2)\cdot CO\cdot C_7H_{14}\cdot CO_2H \xrightarrow{H_2O} C_9H_{19}\cdot NO_2 + C_7H_{14}(CO_2H)_2.$$
$$\text{(II.) } 2C_8H_{17}\cdot CH(O\cdot NO)\cdot CH(NO_2)\cdot C_7H_{14}\cdot CO_2H \longrightarrow H_2O + N_2O +$$
$$C_8H_{17}\cdot CO\cdot CH(NO_2)\cdot C_7H_{14}\cdot CO_2H \longrightarrow C_8H_{17}\cdot CO_2H + NO_2\cdot C_8H_{16}\cdot CO_2H.$$

The action of hydrochloric acid on θ-nitrononoic acid gives rise to azelaic acid: $NO_2\cdot CH_2\cdot[CH_2]_7\cdot CO_2H \longrightarrow$
$$HO\cdot N{:}C(OH)\cdot[CH_2]_7\cdot CO_2H \longrightarrow NH_2\cdot OH + C_7H_{14}(CO_2H)_2.$$
In a similar manner nitrononane yields pelargonic acid.

The above method has been applied to the determination of the position of the double linking in a number of unsaturated compounds. In all cases the unsaturated compound was allowed to combine with nitrogen peroxide in light petroleum solution at a low temperature, and the resulting oily additive compounds were heated with concentrated hydrochloric acid at 130—140°.

Undecenoic acid gave sebacic and formic acids. *iso*Oleic acid decomposes into octoic and sebacic acids, corresponding with the structure $CH_2Me\cdot[CH_2]_5\cdot CH{:}CH\cdot[CH_2]_8\cdot CO_2H$; erucic acid into nonoic and brassylic acids.

From the behaviour of the hexylene, prepared from mannitol, which yielded formic, acetic, butyric and valeric acids, the author draws the conclusion that the hydrocarbon consists of a mixture of two isomerides, $CHMe{:}CHPr^{\alpha}$ and $CH_2{:}CH\cdot CH_2Pr^{\alpha}$.

Methoxy- and ethoxy-undecenoic acids, obtained by the action of alcoholic alkali hydroxides on the dibromide of undecenoic acid, gave results in agreement with the structure:

$$OMe\cdot CH_2\cdot[CH_2]_7\cdot CH{:}CH\cdot CO_2H.$$

The unsaturated acids from linseed oil were also examined and found to consist of a mixture of the two following compounds:

$$CHEt{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H.$$
$$CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H.$$

F. B.

The Theory of the Asymmetric Carbon Atom and Pasteur's Principle. ERNST MOHR (*J. pr. Chem.*, 1912, [ii], **87**, 91—95).—A theoretical paper in which the author shows that, contrary to his previous views (A., 1904, i, 1), a compound of the formula $C(dR)_2(lR)_2$, where dR and lR represent structurally identical, univalent groups of enantiomorphous configuration does not contain an asymmetric carbon atom, and is therefore incapable of existing in two enantiomorphous forms. F. B.

The Melting Point of Ethylene Dibromide. EUGEN VON BIRON (*Zeitsch. physikal. Chem.*, 1913, **81**, 590).—Moles (A., 1912, ii, 533) states that ethylene dibromide has m. p. 9·975°. Biron has shown that when purified by repeated fractional crystallisation it has m. p. 10·012° and D_4^{20} 2·1804 (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1609). He points out that the work must be carried out in the absence of light. J. F. S.

The History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, **37**, 1—2. Compare A., 1912, i, 824).—The author combats the statement attributed to Davidsohn (*Mitt. Ges. Med. Naturwiss.*, 1912, **12**, 102) that the Celts first submitted fermented liquors to distillation and that the knowledge of the process passed from them to other nations. D. F. T.

Ethyl Ether by Catalysis. CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1913, **35**, 93—96).—Sabatier and Mailhe (A., 1910, i, 294) have shown that several metallic oxides, including that of thorium, exert a catalytic action on alcohols between 300° and 350°. In the case of ethyl alcohol, the action appears to consist almost entirely of dehydration with formation of ethylene, but at a lower temperature the dehydration is said to be capable of limitation to the production of ether.

Experiments are described in which alcohol vapour was passed over pure thorium oxide at about 250°, but although the conditions specified by Sabatier and Mailhe were carefully observed, little or no ether was obtained. E. G.

Esters and Amides of the Phosphoric Acids. IV. Reaction between Esters of Metaphosphoric Acid and Uni- and Multivalent Alcohols. Synthesis of Glycero-mono- and -di-phosphoric Acid. Preparation of Pure Silver Metaphosphate. KURT LANGHELD, F. OPPMANN, and E. MEYER (*Ber.*, 1912, **45**, 3753—3760).—In part polemical (compare Grün and Kade, this vol.,

i, 159). When ethyl metaphosphate reacts with ethyl alcohol and benzyl alcohol, the following three products are formed:

$PO(OEt)_2 \cdot O \cdot C_7H_7$, $PO(OH)_2 \cdot O \cdot C_7H_7$, $OEt \cdot PO(O \cdot C_7H_7) \cdot OH$.

The mono- and tri-esters are obtained in molecular proportions. The same result is obtained with glycerol, in which case the excess prevents the determination of the relative proportions of the esters.

Barium glycerophosphate is obtained in stellar aggregates of small platelets containing a molecule of water, which is slowly removed on drying in a vacuum. On exposure of the anhydrous substance, $\frac{1}{2}H_2O$ is absorbed quickly and the second $\frac{1}{2}H_2O$ only slowly. The solubility in water at 220° is 8·4%, and approaches that of the natural product.

Barium glycerodiphosphate, $2H_2O$, crystallises well.

To prepare pure silver metaphosphate, $(AgPO_3)_2,H_2O$, sodium ammonium phosphate is converted into metaphosphate by cautious heating in a vacuum at 320°. About half the product is soluble in water, from which it is precipitated in crystalline form on the addition of alcohol. This product, $2NaPO_3,H_2O$, reacts with silver nitrate.

Silver metaphosphate crystallises in large octahedra. E. F. A.

The Glycerotriphosphoric Acid of Contardi. PAUL CARRÉ (*Compt. rend.*, 1912, **155**, 1520—1521*).—A reply to Contardi (compare A., 1912, i, 743), in which the author maintains that the esterification of 1 mol. of glycerol with 3 mols. of phosphoric acid gives glycerodiphosphoric acid, $C_3H_5(PO_4H_2)_2 \cdot OH$, glycerophosphoric acid, and a di-ester of the form PO_4R_2H, about 50% of the phosphoric acid remaining unaltered and no glycerotriphosphoric acid being formed.

He further maintains his views, already expressed (compare A., 1904, i, 133, 215; 1905, i, 184), that, on heating an equimolecular mixture of glycerol and phosphoric acid in a vacuum, the mixture is transformed quantitatively into the normal tri-ester. W. G.

Crystalline Forms of Salts of Ethanedisulphonic Acid. K. BLEICHER (*Zeitsch. Kryst. Min.*, 1912, **51**, 502—520).—Detailed crystallographic constants are given for the following salts of ethanedisulphonic acid: Sodium ($2H_2O$), monoclinic;

$$a:b:c = 0·7893:1:0·4624;$$

$\beta = 91°34'$. Lithium ($2H_2O$), monoclinic; $a:b:c = 1·5717:1:2·5939$; $\beta = 111°7'$. Potassium, monoclinic; $a:b:c = 1·2594:1:5816$; $\beta = 126°18'$. Ammonium, monoclinic; $a:b:c = 1·1647:1:0·6959$; $\beta = 120°21'$. Potassium sodium ($2H_2O$), rhombic;

$$a:b:c = 0·7467:1:0·5563.$$

Disodium ammonium, $Na_4(NH_4)_2(C_2H_4S_2O_6)_3$, monoclinic; $a:b:c = 1·5637:1:0·5906$; $\beta = 101°17'$. Lithium potassium ($1H_2O$), monoclinic; $a:b:c = 1·2401:1:1·2753$; $\beta = 104°41'$. Lithium ammonium, monoclinic; $a:b:c = 0·7627:1:0·7799$; $\beta = 96°46'$. Barium, rhombic; $a:b:c = 0·7678:1:0·9062$. Barium (H_2O), rhombic; $a:b:c = 0·9374:1:0·4051$. Strontium (H_2O), monoclinic;

$$a:b:c = 0·5347:1:0·0641;$$

$\beta = 101°3'$. Cadmium ($2H_2O$), triclinic; $a:b:c = 1·7421:1:1·0515$. $\alpha = 90°1'$, $\beta = 101°56'$, $\gamma = 100°54'$. Zinc ($3H_2O$), triclinic; $a:b:c =$

* and *Bull. Soc. chim.*, 1913, [iv], **13**, 66—69.

0·5718 : 1 : 0·7813 ; $a = 94°0'$, $\beta = 110°28'$, $\gamma = 90°30'$. Magnesium ($4H_2O$), triclinic ; $a : b : c = 0·6546 : 1 : 0·4066$; $a = 96°18'$, $\beta = 102°9'$, $\gamma = 94°14'$. Copper ($4H_2O$), triclinic ; $a : b : c = 0·6527 : 1 : 0·4350$; $a = 95°15'$, $\beta = 96°39'$, $\gamma = 94°32'$. L. J. S.

Phenomenon of Double Melting for Fats. ANDREAS SMITS and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 681—683).—According to Guth (A., 1903, i, 225), tristearin melts at 71·5°, but if allowed to solidify in a capillary tube it melts at 55°, solidifies again, and melts a second time at 71·5°. In view of the improbable explanation of these results, the authors have made a further examination of the behaviour of the substance, and find that the above phenomena are due to the existence of two crystalline modifications. Of these, the metastable form appears most readily. If, however, the liquid is kept for some time at a temperature between the two melting points, the stable form crystallises out, although very slowly.

When the metastable form is heated, it melts at 54·5°, and when the temperature is then raised to 63° the stable form is deposited. The stable unary melting point is 70·8°. It is probable that the double melting phenomena, observed for other fats, are to be explained in the same way. H. M. D.

Anomalies in the Consistency and Melting Points of Fats. ADOLF GRÜN (*Ber.*, 1912, **45**, 3691—3701).—It has already been observed that glycerides can exist in two modifications (Kast, A., 1906, i, 922 ; Grün and Schacht, A., 1907, i, 462). To this phenomenon is attributable the variation in the m. p. recorded for certain fats with the age or method of preparation of the sample. The present investigation endeavours to extend the present limited knowledge of this phenomenon.

[With A. CUSTODIS].—$\alpha\gamma$-Dilaurin, obtained from $\alpha\gamma$-dichlorhydrin and potassium laurate, is a mixture of two modifications ; the product of higher m. p., 57°, *acetyl* derivative, m. p. 34°, or after one year 32°, is obtained in better yield the lower the reaction temperature (140—150°), whilst the other modification, m. p. 40°, preponderates when the temperature of formation is somewhat higher (170—180°) ; the latter modification very easily remains in a supercooled condition. Both forms, on keeping, finally attain a m. p. 45°, which is also the temperature observed for a mixed m. p. It is probable that the two substances are structurally identical.

When the two forms of $\alpha\gamma$-dilaurin are treated with lauryl chloride at 100°, two modifications of trilaurin are obtained, one m. p. 45°, the other forming soft needles which melt in the hand. The former, obtained from the less fusible dilaurin, is identical with natural trilaurin ; the latter, obtained from the more fusible dilaurin, resembles its parent substance in having in benzene a molecular weight only one-half that expected from the formula ; the less fusible di- and tri-laurins are of normal molecular weight.

$\alpha\gamma$-Dibenzoin, $OBz·CH_2·CH(OH)·CH_2·OBz$, by warming with glycerol and sulphuric acid, can be converted into a modification

which remains oily at the ordinary temperature; the molecular weight of the substance in benzene solution is, however, approximately normal.

αβ-Dibenzoin, obtained from anhydrous potassium benzoate and αβ-dibromohydrin, and also in a purer condition by the use of silver benzoate, is also a viscous, uncrystallisable oil.

In an addendum it is remarked that lack of recognition of the above peculiarities of glycerides may lead to considerable errors, as, for example, the reported formation of αβ-dilaurin from αγ-dichlorohydrin (van Eldik Thieme, A., 1912, i, 333). D. F. T.

The Synthesis of Fats. DAVID HOLDE (*Ber.*, 1912, 45, 3701—3702. Compare Kremann and Schoulz, A., 1912, ii, 1152).—The author draws attention to the manner in which the results of Kremann and Schoulz (*loc. cit.*) support his views (A., 1903, i, 140) that the stearic and palmitic acids in olive oil must be present in the form of "mixed" glycerides, and not as tripalmitin and tristearin.

D. F. T.

Diglyceride-phosphoric Acids. ADOLF GRÜN and FRITZ KADE (*Ber.*, 1912, 45, 3358—3367).—When phosphoric oxide acts on distearin at temperatures above 100°, or in the absence of moisture, blackening takes place. When the requisite amount of water is added, esters of pyrophosphoric acid or primary orthophosphoric acid esters are obtained. The former decompose into phosphoric acid and the ortho-acid esters, which are transformed in turn into secondary and tertiary esters and finally into the stable form, pentadistearin phosphate. In addition the reaction product contains free phosphoric acid and distearin. The changes are expressed by the scheme:

$$PO(OR)(OH)\cdot O\cdot PO(OH)_2 \longrightarrow PO(OR)(OH)_2 \longrightarrow PO(OR)_2(OH) \longrightarrow PO(OR)_3 \longrightarrow P(OR)_5.$$

αβ-Distearin pyrophosphate, $C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot P_2H_3O_6$, is a colourless, crystalline, fatty substance, m. p. about 65°; primary *αβ-distearin orthophosphate* forms colourless, somewhat lustrous, matted crystals, m. p. 71°. The *secondary* ester yields soft crystals, m. p. about 67°; it forms a waxy, pale yellow *silver* salt with silver acetate, and a *potassium* salt separating in colourless platelets. The *tertiary* ester is very similar to the other esters, but the solution is neutral.

Pentadistearin phosphate, $P[O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2]_5$, forms colourless, brittle crystals, m. p. 70°. All the compounds described are very ill-defined. E. F. A.

Alleged Synthesis of Lecithins. ADOLF GRÜN and FRITZ KADE (*Ber.*, 1912, 45, 3367—3376).—To effect the synthesis of lecithins it is proposed to allow the components of choline to act in turn on diglyceride-phosphoric acid. Ethylene glycol and phosphoric oxide acting on distearin produce almost quantitatively *distearin ethylene-glycol orthophosphate*,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4\cdot OH.$$

When ethylene chlorohydrin is used, the reaction takes place in two directions, the glycol ester as well as the *β-chloroethyl* ester,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4Cl,$$

being formed. This compound reacts with trimethylamine, forming the *trimethylammonium* salt,

$$C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2{\cdot}O{\cdot}PO(O{\cdot}C_2H_4Cl){\cdot}O{\cdot}NHMe_3,$$

and on more energetic action of excess of trimethylamine this undergoes rearrangement to lecithin hydrochloride,

$$C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2{\cdot}O{\cdot}PO(O{\cdot}C_2H_4{\cdot}NMe_3Cl){\cdot}OH.$$

The final product obtained was a mixture of both compounds together with an intermediate product.

The *β-chloroethyl* ester, from αβ-distearinphosphoric acid, forms colourless crystals, which sinter at 60°, m. p. 65—66°; the isomeric αγ-distearin compound is very similar.

The *ethyleneglycol* ester of *αβ-distearinphosphoric* acid has m. p. 65—70°, and is a typically fatty substance. It reacts faintly acid.

The *trimethylammonium* salt forms tough crystals which sinter at 60°, m. p. 69°.

The synthetic lecithin hydrochloride (αβ-distearincholinephosphoric acid ester) product is a soft, waxy compound, which sinters at 60° to a clear, viscid oil, which becomes mobile at 64—65° and opaque at 74°.

E. F. A.

Preparation of Mixed αβ-Diglycerides. ADOLF GRÜN and B. SCHREYER (*Ber.*, 1912, **45**, 3420—3426).—Glycerol-α-monochlorohydrin is converted by the action of myristoyl chloride into the ester, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{13}H_{27}$, which reacts with stearyl chloride to form myristostearochlorohydrin,

$$CH_2Cl{\cdot}CH(O{\cdot}CO{\cdot}C_{17}H_{33}){\cdot}CH_2(O{\cdot}CO{\cdot}C_{13}H_{27}).$$

On treatment with silver nitrite the chlorine atom is replaced by hydroxyl and α-myristo-β-stearin obtained.

α-Myristo-γ-chlorohydrin is a yellow, mobile oil; it is converted by silver nitrite into α-monomyristin, m. p. 68°.

β-Myristo-αγ-dichlorohydrin forms colourless, transparent, glass-like crystals, m. p. 20°. The *β-monomyristin* obtained from it gives colourless, lustrous, crystalline plates, m. p. 69°.

α-Myristo-β-stearo-γ-chlorohydrin forms colourless crystals, m. p. 31°.

α-Myristo-β-stearin crystallises in slender platelets, m. p. 58°.

E. F. A.

Alcoholysis and the Composition of Cocoanut Oil. GEORGE D. ELSDON (*Analyst*, 1913, **38**, 8—11).—Cocoanut oil when boiled in a reflux apparatus with absolute methyl alcohol containing 2% of hydrogen chloride for about twenty hours deposits on cooling a large quantity of methyl esters; the remainder may be obtained by diluting the alcoholic solution with water and agitating with ether.

When the mixture of the esters is submitted to distillation at 14 mm. pressure, seven fractions may be isolated (b. p. 63—76°, 76—100°, 100—128°, 128—153°, 153—182°, 182—204°, 204—216°).

From the results obtained on weighing, refractionating, and further identification of the fractions, the author considers that the composition of the fatty acids and of cocoanut oil may be represented approximately

by hexoic acid 2%, octoic acid 9%, decoic acid 10%, lauric acid 45%, myristic acid 20%, palmitic acid 7%, stearic acid 5%, and oleic acid 2%.
L. DE K.

Preparation of Ethyl Acrylate. FREDERICK G. TROBRIDGE (*Proc. Univ. Durham, Phil. Soc.*, 1912, 4, 223—224).—Ethyl acrylate is obtained in 80% yield by the action of the zinc-copper couple on ethyl $\alpha\beta$-dibromopropionate in ethereal solution.
F. B.

Action of Zinc on a Mixture of Pinacolin and Ethyl α-Bromopropionate. NICOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1776—1788).—This incomplete investigation is published owing to the appearance of Umnova's paper (this vol., i, 7), and is a continuation of work begun by Lazarkevitsch and proceeded with by Reformatski and Agafonov.

The products of the action of zinc on a mixture of pinacolin (1 mol.) and ethyl bromopropionate (1 mol.) vary with the conditions of the reaction. If the latter takes place at the ordinary temperature and the viscous mass obtained after three or four days is decomposed with water, a yield of 30% of ethyl β-hydroxy-$\alpha\beta\gamma\gamma$-tetramethylvalerate is obtained. At 50—70°, however, this ester is accompanied by (1) a lactone, $C_9H_{16}O_2$, which may also be obtained by boiling either the ester or the corresponding acid for some hours with 20% sulphuric acid solution; (2) ethyl propionylpropionate, which yields diethyl ketone on hydrolysis.

β-Hydroxy-αβγγ-tetramethylvaleric acid,

$$CMe_3\cdot CMe(OH)\cdot CHMe\cdot CO_2H,$$

forms large, colourless crystals (? rhombohedra), m. p. 109·5—110·5°, and has the normal molecular weight in freezing acetic acid. Its *ethyl ester*, $C_{11}H_{22}O_3$, is a colourless, viscous liquid, b. p. 117°/20 mm., D_4^{20} 0·96034, n_D^{20} 1·44039, and exhibits normal cryoscopic behaviour in benzene. The *potassium, barium, calcium* (+ H_2O), and *silver* salts were analysed.

The *lactone*, $CMe_3\cdot CH<\begin{matrix}CHMe\cdot CO\\ CH_2—O\end{matrix}$ or $CMe_2<\begin{matrix}CHMe\cdot CO\\ CMe_2—O\end{matrix}$, forms large crystals, m. p. 65—66°, and exhibits the normal molecular weight in freezing acetic acid; when boiled with water it yields a neutral solution and does not combine with it.
T. H. P.

Uranium Salts. ARRIGO MAZZUCCHELLI and OLGA GRECO D'ALCEO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 620—626).—The paper deals with complex uranium salts. Additive products are practically not formed in the following cases: mercuric cyanate, carbamide or thiocarbamide with uranyl nitrate; carbamide or hexamethylenediamine with uranyl oxalate; hexamethylenediamine, aniline or pyridine with the complex sodium uranyl pyrophosphate, malonate or succinate. Attempts to prepare complex salts from aminoacetic, aspartic, aminobenzoic and sulphanilic acids were unsuccessful. The *aspartate*,

$$UO_2(C_4H_6O_4N)_2,3H_2O,$$

was prepared, but it is not a complex derivative. The *aminobenzoate*, $UO_2(C_7H_6O_2N)_2,4H_2O$, was obtained, and also the basic *sulphanilate*, $UO_3\cdot C_6H_7O_3NS,H_2O$.

The uranous salts also appear to have little tendency to form aminic

complexes. Diurano-oxalic acid gives ordinary *salts* with *pyridine* $[2U(C_2O_4)_2\cdot C_2O_4(C_5H_5N)_2]$ and with *aniline* $[2U(C_2O_4)_2\cdot C_2O_4(C_6H_7N)_2]$. Indications were obtained of the formation of a complex salt in the case of uranous aminoacetate. The basic *succinate*, $UO\cdot C_4H_4O_4,2H_2O$, was prepared, and also the analogous *malonate*, $UO\cdot C_3H_2O_4,6H_2O$. When a solution of sodium uranylmalonate with an excess of malonic acid is electrolytically reduced, the anodic liquid being an acid solution of sodium malonate separated from it by a parchment, dark green, dichroic crystals of the complex *salt*, $U(C_3H_2O_4)_3Na_2,2H_2O$, are obtained on subsequent concentration of the cathodic liquid in a vacuum. A basic *uranous phthalate*, $UO:C_8H_4O_4,3H_2O$, and *uranous trichloroacetate*, $UO(C_2O_2Cl_3)_2,3H_2O$, were also prepared.

R. V. S.

Molecular Rearrangements in the Camphor Series. XI. Derivatives of *iso*Camphoric Acid: *iso*Aminocamphonanic Acid and Its Decomposition Products. WILLIAM A. NOYES and LEONIDAS R. LITTLETON (*J. Amer. Chem. Soc.*, 1913, **35**, 75—81).—It has been shown in earlier papers (A., 1895, i, 295; 1909, i, 133) that aminocamphonanic acid (aminolauronic acid) is decomposed by nitrous acid with formation of lauronolic acid, laurolene, and *iso*campholactone. The present work was undertaken with the object of preparing *iso*aminocamphonanic acid and studying its behaviour with nitrous acid.

sec.-Methyl *iso*camphorate (α-methyl *iso*camphorate),

$$CO_2H\cdot C_8H_{14}\cdot CO_2Me,$$

has m. p. 89·5—90°, and $[\alpha]_D$ $-58·4°$ in 10% alcoholic solution (compare Noyes and Knight, A., 1911, i, 111). The tert.-*methyl* ester, prepared by boiling a solution of the dimethyl ester in methyl alcohol with sodium hydroxide, was obtained as a very viscous oil; it has $[\alpha]_D$ $-53·1°$ in 10% alcohol solution. The terms "secondary" and "tertiary" are used here to indicate the carboxyl containing the methyl group.

Methyl sec.-iso*camphoramate*, $CO_2Me\cdot C_8H_{14}\cdot CO\cdot NH_2$, m. p. 126—127°, prepared from the *sec.*-methyl ester by converting it into the chloride and treating the latter with ammonia, crystallises in rectangular plates, and has $[\alpha]_D$ $-54·1°$ in 10% solution in methyl alcohol. When this ester is warmed with sodium hypobromite solution it yields *methyl* iso*aminocamphonanate*, b. p. 239° (corr.), m. p. 230° (decomp.), which forms white crystals; the *hydrochloride*,

$$CO_2Me\cdot C_8H_{14}\cdot NH_2,HCl,H_2O,$$

has $[\alpha]_D$ $-32·03°$ in 10% solution in water, and $-42·03°$ in 10% solution in alcohol. If this hydrochloride is warmed with solution of sodium hydroxide and subsequently acidified with hydrochloric acid, the *hydrochlo ide* of iso*aminocamphonanic acid*,

$$\begin{array}{l} CH_2-CH_2 \\ \vert \\ NH_2\cdot CH\cdot CMe_2 \end{array}\!\!>CMe\cdot CO_2H,HCl,$$

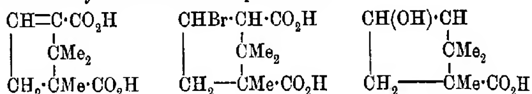
m. p. 320° (corr.), is obtained, which is decomposed by nitrous acid with formation of *cis*-camphonolactone, together with small quantities of an unsaturated *acid*, b. p. 150°/60 mm. (decomp.), and a saturated acid which decomposes at 160°.

E. G.

New Methods of Preparation of Camphonenic (γ-Lauronolic) Acid and the Relation of the Latter to Laurolenic (Lauronolic) Acid. JULIUS BREDT [and, in part, PAUL LEVY and S. LINK] (*J. pr. Chem.*, 1913, [ii], 87, 1—11).—The first part of this paper is mainly a summary of the authors' views on the constitution and relationships of the lauronolic acids and allied compounds, together with suggestions concerning their nomenclature (compare A., 1911, i, 417).

When submitted to slow distillation, dehydrocamphoric acid (A., 1902, i, 374) loses carbon dioxide, yielding γ-lauronolic (camphonenic) acid (I). It is accompanied by *iso*dehydrocamphoric anhydride, from which it may be separated by distillation in steam. When purified by the calcium salt, $C_{18}H_{26}O_4Ca,H_2O$, and repeatedly crystallised from dilute acetic acid it is obtained in feather-like crystals, m. p. 155—156° (compare Noyes, A., 1912, i, 159).

Dehydrocamphoric acid combines with hydrobromic acid, yielding a mixture of two stereoisomeric *hydrobromides* (II), of which the *cis*-form has m. p. 168—170°, and is reduced by zinc and acetic acid to *cis*-camphoric acid, whilst the *cis-trans*-modification has m. p. 232°, and on reduction yields *cis-trans*-camphoric acid:



(I.) (II.) (III.)

When boiled in aqueous solution the sodium salt of the *cis-trans*-hydrobromide yields as main product a *hydroxy-acid* (III), which is accompanied by γ-lauronolic acid (10%).

Oxidation of γ-lauronolic acid with nitric acid, or of its calcium salt with potassium permanganate, gives rise to camphoronic acid. F. B.

A New Method of Preparation of Laurolenic (Lauronolic) Acid and the Decomposition of Camphanic Acid in an Electric Reflux Heater under Diminished Pressure. JULIUS BREDT and AUGUST AMANN (*J. pr. Chem.*, 1913, [ii], 87, 12—26).—Lauronolic acid, which the authors now terms laurolenic acid, is obtained by boiling γ-camphonanic acid (A., 1912, i, 113) for a short time with aqueous sodium carbonate. It is accompanied by camphonololactone, and has also been prepared (1) by distillation of camphanic acid under diminished pressure in a specially constructed, electrically heated apparatus, a sketch of which is given, and (2) by heating chlorocamphoric anhydride (A., 1912, i, 411) with aqueous sodium carbonate. The m. p. of the acid varies from 5·5—7° to 8·5—10° according to its method of preparation, and $[\alpha]_D$ from 181·3° to 195·2°.

The calcium salt separates from its aqueous solution at the ordinary temperature with $2H_2O$, and not $3H_2O$, as stated by Noyes and Burke (A., 1912, i, 159). F. B.

Methods for the Preparation of Neutral Solutions of Ammonium Citrate. JAMES M. BELL and CHARLES F. COWELL (*J. Amer. Chem. Soc.*, 1913, 35, 49—54).—The methods at present

employed for the preparation of neutral solutions of ammonium citrate are not satisfactory and two new methods have therefore been devised. In one of these methods, the excess of ammonia is estimated by extracting the solution with chloroform, and titrating the chloroform with $0{\cdot}1N$-hydrochloric acid in presence of methyl-red as indicator. In the other method, the rise of temperature due to the heat of neutralisation is observed as the citric acid solution is titrated with ammonia, the end-point being at the break in the heating curve. Both these methods are considered to be simpler than that involving the determination of the conductivity of solutions at constant temperature.

E. G.

Thio-γ-valerolactone. KARL FRIES and H. MENGEL (*Ber.*, 1912, 45, 3408—3411).—On heating valerolactone with phosphorus pentasulphide, *thio-γ-valerolactone*, $CHMe<\begin{matrix}CH_2\cdot CH_2\\ S\text{---}CO\end{matrix}$, is obtained as a colourless oil of pleasant aromatic odour, b. p. 94—95°/20 mm. It is readily hydrolysed by alkali hydroxides to γ-mercaptovaleric acid, which is reconverted into the thiolactone on treatment with mineral acids.

A further product of the action of the pentasulphide is *dithio-γ-valerolactone*, $CHMe<\begin{matrix}CH_2\cdot CH_2\\ S\text{---}CS\end{matrix}$, an orange-coloured, viscid oil of unpleasant odour. Condensing agents such as sodium methoxide convert it very readily into *trithio-di-γ-valerolactone*,

$$CHMe<\begin{matrix}CH_2\cdot CH_2 & CS\cdot S-\\ S\text{---}C & =\!\!=C\cdot CH_2\end{matrix}>CHMe,$$

which crystallises in bunches of large, red prisms, m. p. 77°.

E. F. A.

Maleindialdehyde. ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, 45, 1746—1756).—Maleindialdehyde diethylacetal, an intermediate product in the preparation of tartardialdehyde (A., 1912, i, 162), has been hydrolysed by means of dilute sulphuric acid, and the maleindialdehyde has been characterised. The most striking property of this compound is its yellow colour, which is more intense than that of diacetyl and may be accounted for by the grouping together of conjugated double bonds and the conveying of the influence of one carbonyl group to the other by an ethylenic linking. Oxidation by silver carbonate gives maleic and also fumaric acids, and since the original acetal yields a tartardialdehyde acetal of the type of mesotartaric acid (*ibid.*), it is suggested that this is the real maleindialdehyde, whereas that obtained by Marquis from nitrosuccinaldehyde monoacetin (A., 1905, i, 224) is fumardialdehyde, especially as the nitrous acid which is formed at the same time has a great tendency to convert maleic into fumaric acid.

For the preparation of *maleindialdehyde*, $CHO\cdot CH{:}CH\cdot CHO$, 35 grams of the acetal are shaken with 150 c.c. of $N/10$-sulphuric acid and the faintly yellow, pungent smelling solution is exactly neutralised with barium hydroxide. After removing the barium sulphate by centrifugation, the solution is evaporated at 40° in a vacuum with a

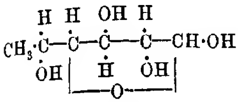
fractionating column which, however, does not prevent the loss of some aldehyde, since it is volatile in steam, and the residue is extracted with chloroform and dried. The extract is evaporated in the same way and the syrupy residue is maintained at 105—115°/9 mm., when the polymeric substances slowly decompose and the aldehyde distils over. The distillate is collected in a Claisen flask in a freezing mixture and redistilled from a bath already heated to 75°, when the mobile, yellow, pungent-smelling aldehyde boils at 56—59°/9·5 mm. It dissolves in water and organic solvents, and probably forms hydrates and alcoholates, since yellow aqueous or alcoholic solutions soon become colourless. It is only slowly affected by oxygen or bromine water, but it immediately reduces permanganate or ammoniacal silver oxide. At the ordinary temperature it very quickly changes to a syrup with less intense colour and odour, and it is then only slightly soluble in ether, benzene or warm water. From the aqueous solution an amorphous solid separates out; probably a syrupy and a solid polymeride exist.

Derivatives of the dialdehyde have been prepared by hydrolysing the acetal, exactly neutralising with sodium carbonate, and precipitating with the free base in the cold. The *diphenylhydrazone*, NHPh·N:CH·CH:CH·CH:N·NHPh, forms unstable, yellow, quadratic leaflets from hot alcohol, m. p. 198—199°; Marquis's dihydrazone melts at 236—237° (*ibid.*). It gives a reddish-violet compound on oxidation, which is similar to, but not identical with, Marquis's "tetrazone"; they are probably not tetrazones at all. The *dioxime*, $C_4H_6O_2N_2$, forms pure white needles from hot methyl alcohol which decompose with violence at 150—155°; Marquis's compound decomposes at 220° (*ibid.*). The *disemicarbazone*, $C_6H_{10}O_2N_6$, is only very slightly soluble, and crystallises best from a large volume of boiling water in slender needles, m. p. 246—247° (corr.). J. C. W.

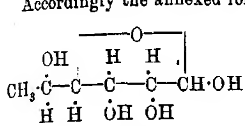
The Isomeric Changes of Dextrose Produced by Alkalis. Theory of Catalytic Action. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1912, 47, 447—461).—The changes in dextrose (measured chiefly polarimetrically) produced by alkalis (in presence of phosphates, etc., added to keep the hydrogen-ion concentration constant during the experiment) is directly proportional to the hydroxyl-ion concentration. The acid nature of dextrose was demonstrated, and its dissociation constant was found to be $5 \cdot 10^{-13}$. This was measured by ascertaining the changes in the hydroxyl-ion concentration of sodium hydroxide solutions (measured electrometrically) produced by the addition of dextrose. From these facts, the hypothesis is put forward, that the "catalytic" action of the hydroxyl ions increases the number of sugar ions, according to theory of mass action, and it is the latter which spontaneously undergo isomeric change. S. B. S.

Conversion of *d*-Glucose [Dextrose] into a Methylpentose. EMIL FISCHER and KARL ZACH (*Ber.*, 1912, 45, 3761—3773).—Triacetylmethylglucoside bromohydrin (Fischer and Armstrong, A., 1902, i, 263), $CH_2Br\cdot CH(OAc)\cdot\underbrace{CH\cdot CH(OAc)\cdot CH(OAc)\cdot CH(OMe)}_{O}$,

is converted on reduction with acetic acid and zinc dust into a triacetyl derivative which on alkaline hydrolysis yields *β-methyl*-d-*isorhamnoside*, $CH_3\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot OMe$. This is hydrolyed by acids to *d-iso*rhamnose (annexed formula), which is identical with the *iso*rhodeose described by Votoček (A., 1911, i, 354), and obtained by him from purgic acid. Since no asymmetric carbon atom is concerned in the series of reactions, no Walden rearrangement is possible, and the methylpentose has the same configuration as *d*-glucose.



Accordingly the annexed formula of *l*-rhamnose (methyl-*l*-mannose), which was hitherto uncertain, is established.



β-Methyl-*d*-*iso*rhamnoside, like *β*-methylglucoside, is hydrolysed by emulsin, whereas *β*-methylxyloside is not attacked. Renewed emphasis is laid on this remarkable difference in view of the similarity in structure of the three glucosides.

Triacetyl-methyl-d-*isorhamnoside* crystallises in well-formed, colourless needles, m. p. 100° (corr.), $[\alpha]_D^{20}$ − 20·22°.

β-Methyl-d-*isorhamnoside* forms slender, colourless needles, m. p. 133° (corr.), $[\alpha]_D^{20}$ − 55·3°, which taste bitter.

*d-iso*Rhamnose separates in hard, colourless crystals in a variety of forms, m. p. 139—140° (corr.). The rotation changes from $[\alpha]_D^{20}$ + 73·3° to + 29·7° in aqueous solution.

*d-iso*Rhamnosephenylosazone crystallises in yellow needles, m. p. 185° (corr.), to a dark red liquid (compare Votoček, *loc. cit.*), $[\alpha]_D^{20}$ − 95° in white light; it is the optical antipode of *l*-rhamnosephenylosazone.

*d-iso*Rhamnonolactone has m. p. 151—152° (corr.), $[\alpha]_D^{20}$ changing from + 66·88° to + 5·35°.

E. F. A.

Properties of Phytin. M. A. Egorov (*Bied. Zentr.*, 1912, **42**, 66—67; from *J. Exper. Landw.*, 1912, **12**, 361).—The phosphoric acid of phytin, which is precipitated by acid molybdate solution, is not precipitated under ordinary conditions in ammonium citrate solution by magnesia mixture.

When phytin is boiled with water for fourteen to sixteen hours it is completely decomposed with production of inositol and inorganic phosphoric acid compounds. The yield of phosphoric acid is about 100%.

N. H. J. M.

Formation of Humus and Combustible Minerals without the Intervention of Atmospheric Oxygen, Micro-organisms, High Temperatures, or Great Pressure. Louis C. Maillard (*Compt. rend.*, 1912, **155**, 1554—1556).—A theoretical discussion of work previously described (compare A., 1912, i, 13, 169). The author has now shown that oxidation does not intervene in any way in

the generation of carbon dioxide and the production of humic substances by the interaction of sugars and amino-acids. He has further obtained a jet black substance, rich in carbon and containing nitrogen, which exhibits a remarkable resistance to reagents, and he suggests that this reaction should be taken into account in framing theories as to the formation of combustible minerals. W. G.

Some Unstable Nitrites Fixed by means of Organic Bases. III. GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 640—643).—The author describes stable compounds of the nitrites of mercury, zinc, and cadmium with hexamethylenetetramine. The substances were prepared by adding sodium nitrite to a solution of a salt of the metal in the presence of hexamethylenetetramine. The *compound*, $2Hg(NO_2)_2,8H_2O,3C_6H_{12}N_4$, forms white crystals with a greenish lustre. The *compound*, $Zn(NO_2)_2,2H_2O,C_6H_{12}N_4$, forms colourless prismatic crystals, as does also the *compound*, $Cd(NO_2)_2,2H_2O,C_6H_{12}N_4$. R. V. S.

Alloxan Anhydride and Its Methyl Derivatives. HEINRICH BILTZ (*Ber.*, 1912, 45, 3659—3675).—By heating under reduced pressure it is found possible completely to dehydrate alloxan and its methyl and dimethyl derivatives; the anhydrous substances have an intense yellow colour and can be sublimed unchanged in a vacuum.

Alloxan anhydride, $C_4H_2O_4N_2$, obtained by heating the monohydrate for an hour at 210—220° in a vacuum produced by a mercury pump, forms yellow, rhombic crystals ($a:b:c = 0.9974:1:1.6841$), m. p. 256° (decomp.). A partial dehydration of the monohydrate is also effected by recrystallising from acetic acid.

Methylalloxan anhydride, obtained from the monohydrate by similar treatment to the previous but at 160°, separates from acetic acid in leafy crystals (rhombic system, $a:b:c = 0.6766:1:?$), m. p. 154—156° (decomp.).

Dimethylalloxan anhydride (compare Holleman, A., 1897, i, 599) could be obtained from the monohydrate by heating in a water-pump vacuum at 210—220°; it crystallises from benzyl cyanide in short, yellow columns (rhombic system, $a:b:c = 0.6847:1:?$).

[With E. TOPP.]—The above anhydrous compounds separated from alcohols containing a little hydrogen chloride in the form of alcoholates which are analogous to the phenolates described earlier (Boehringer & Söhne, D.R.P. 1898, 107720; 1899, 113722). *Alloxan ethyl alcoholate*, $CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>C(OH)\cdot OEt$, prisms; *alloxan methyl alcoholate*, prisms; *alloxan benzyl alcoholate*, prisms.

Methylalloxan ethyl alcoholate, tablets.

Dimethylalloxan ethyl alcoholate, tetragonal prisms, m. p. 95°; *dimethylalloxan methyl alcoholate*, m. p. *circa* 90°, hexagonal tablets; *dimethylalloxan benzyl alcoholate*, crystals, m. p. 185—188°.

All these alcoholates when heated eliminate the molecule of alcohol, giving a residue which has approximately the m. p. of the pure anhydride.

The following compounds were prepared by crystallisation from a

solution of the anhydride and a phenol with hydrogen chloride in acetic acid; *alloxan phenolate*, decomposing at 240—245°; alloxan *p*-cresolate decomposing at 228—230° (compare Boehringer & Söhne, *loc. cit.*); *dimethylalloxan* p-*cresolate*, hexagonal prisms, m. p. 105°.

[With J. KARTTE.]—An aqueous solution of dimethylalloxan dihydrate when saturated with sulphur dioxide and evaporated in a vacuum desiccator deposits *dimethylalloxan sulphite*,

$$CO\!<\!\begin{matrix}NMe\cdot CO\\ NMe\cdot CO\end{matrix}\!>\!C(OH)\cdot SO_3\cdot C(OH)\!<\!\begin{matrix}CO\cdot NMe\\ CO\cdot NMe\end{matrix}\!>\!CO,$$

colourless prisms, which decompose at 75°. *Methylalloxan sulphite*, obtained in an analogous manner, crystallises in prisms with $4H_2O$. *Alloxan sulphite* forms rhombic leaflets, decomposing near 184°.

Alloxan anhydride condenses in alcoholic acetic acid solution with dimethylcarbamide producing 7 : 9-dimethyluric acid glycol (compare Biltz and Krebs, A., 1910, i, 526), but the product from dimethylalloxan anhydride and dimethylcarbamide was allocaffeine (compare Biltz and Krebs, *loc. cit.*, i, 521).

Working details are given of the methods found most suitable for the preparation of di- and tetra-methylalloxantin and their conversion into methyl- and dimethyl-alloxans. D. F. T.

The System Ammonium Thiocyanate–Thiocarbamide–Water. ANDREAS SMITS and A. KETTNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 683—686).—The investigation of the melting-point diagram of the pseudo-binary system ammonium thiocyanate–thiocarbamide has given results which indicate the existence of a compound $NH_4CNS,4CS(NH_2)_2$, whereas Atkins and Werner (T., 1912, 101, 1167) are of the opinion that the compound has the composition $NH_4CNS,3CS(NH_2)_2$. The evidence for the former is supported by the results of the determination of the solubility isotherms at 25° and the examination of the co-existing solid phases by the residue method. The solubility curves afford a simple explanation of the method of preparation of thiocarbamide from ammonium thiocyanate recommended by Reynolds and Werner (T., 1903, **83**, 1), which up to the present has not been satisfactorily accounted for. H. M. D.

Selective Catalysis of Dehydrogenation. NICOLAI D. ZELINSKI (*Ber.*, 1912, **45**, 3678—3682).—The catalytic dehydrogenation of *cyclo*hexane compounds by palladium or platinum at 300° and the inactivity of these metals towards *cyclo*pentane compounds under the same conditions can be applied to the separation of *cyclo*hexane and *cyclo*pentane hydrocarbons.

[With (Frl.) A. HERZENSTEIN.]—After a mixture of equal volumes of methyl*cyclo*pentane and *cyclo*hexane has been thrice submitted to the action of platinum black at 300°, no further liberation of hydrogen occurs, and the hydrogen collected amounts to more than 90% of the theoretical. After removal of the benzene from the resultant hydrocarbon mixture by treatment at the ordinary temperature with sulphuric acid (two volumes of acid, D 1·84, mixed with one volume of fuming acid containing 7% of anhydride), the residual liquid was pure methyl*cyclo*pentane.

*cyclo*Heptane resembles *cyclo*pentane (Zelinski, A., 1911, i, 958) in resisting the above catalytic dehydrogenation.

A specimen of naphtha, b. p. 102—104°, D^{18} 0·7647, n^{18} 1·4215, from Baku petroleum, by the above treatment gave a liquid which could be separated by distillation into two fractions. The less volatile fraction, b. p. 105—107°, contained much toluene, whilst the other fraction, b. p. 104—105°, after one more treatment with platinum black followed by the removal of any aromatic hydrocarbons by means of the special sulphuric acid mentioned above, gave a hydrocarbon, C_7H_{14}, b. p. 101—102·5°/747 mm., D_4^{20} 0·7488, n^{20} 1·4101, which is probably a *cyclo*pentane or *cyclo*butane derivative.

[With W. Dobrochotov.]—Another specimen of naphtha, b. p. 100—100·5°, D^{18} 0·766, $n^{20.5}$ 1·4210, when submitted to the action of platinum black at 300°, liberated much hydrogen, and after the removal of toluene and redistillation had b. p. 100—101°, D_4^{18} 0·7490, n^{18} 1·4142. The original hydrocarbon, a "heptanaphthene," which had been previously treated with a mixture of nitric and sulphuric acids, had therefore yielded a *cyclo*paraffin product very similar to that obtained from the above naphtha fraction (b. p. 102—104°), which had not been first treated with nitric and sulphuric acids. D. F. T.

Formation of Dimethylstyrene [β-Phenyl-Δ^{β}-butylene] from Phenyldimethylethyl Alcohol [β-Phenyl*iso*butyl Alcohol]. Albin Haller and Édouard Bauer (*Compt. rend.*, 1912, 155, 1581—1585).—By the action of sodamide on phenylacetonitrile (1 mol.) in ethereal solution followed by the addition of methyl iodide (1 mol.), a liquid, b. p. 115—120°/19—20 mm., is obtained, which on further treatment with sodamide and methyl iodide gives α-phenyl*iso*butyronitrile (compare Wallach, A., 1900, i, 229). This substance on hydrolysis with 85% sulphuric acid on a water-bath furnishes the corresponding amide, which by reduction with sodium in absolute alcohol yields *β-phenyl*iso*butyl alcohol*, $CPhMe_2\cdot CH_2\cdot OH$, b. p. 122—123°/20 mm., which gives a *phenylurethane*, white needles, m. p. 59—60°. During the reduction there is produced at the same time some β-phenyl*iso*butylamine, b. p. 115—116°/20 mm. (compare Wallach, *loc. cit.*), which forms a *platinichloride*, insoluble in water.

By acting on β-phenyl*iso*butyl alcohol with thionyl chloride in slight excess at 0°, a liquid is obtained separable into two fractions, of which one is β-phenyl-Δ^{β}-butylene, CPhMe:CHMe (compare Klages, A., 1902, i, 666; 1903, i, 19), and the other a *chloride*, $C_{10}H_{13}Cl$, b. p. 104—105°/20 mm., the constitution of which has not yet been established. With silver acetate, it gives an *acetate*, which on saponification gives an *alcohol*, b. p., 115—117°/15 mm., isomeric with the alcohol from which the chloride was derived. W. G.

2:4:6-Tribromo-1-iodo-3-nitrobenzene. C. Loring Jackson and Webster N. Jones (*Amer. Chem. J.*, 1913, 49, 46—55).—2:4:6-Tribromo-3-nitroaniline (Körner, A., 1876, i, 210) has m. p. 101·5°; Remmers (A., 1874, 696) assigned the m. p. 214—215° to this compound, but it is now shown that his substance was probably 2:4:6-tribromo-3-nitroacetanilide. 2:4:6-Tribromo-3-nitrodiacetanilide

(Remmers, *loc. cit.*) has m. p. 168—169°, and seems to be identical with the substance supposed by Wheeler (A., 1896, i, 157) to be the monoacetanilide. 2 : 4 : 6-*Tribromo-3-nitroacetanilide*, m. p. 208—209°, forms white, rhombic crystals.

2 : 4 : 6-*Tribromo-1-iodo-3-nitrobenzene*, $C_6HBr_3I \cdot NO_2$, m. p. 144—145°, obtained by the action of potassium iodide on the diazotisation product of 2 : 4 : 6-tribromo-3-nitroaniline, crystallises in white, rectangular plates. When this substance is treated with a solution of sodium ethoxide, it is converted into a *dibromoiodonitrophenetole*,

$$NO_2 \cdot C_6HBr_2I \cdot OEt,$$

m. p. 121°, which forms long, white, rectangular prisms; other compounds are produced in this reaction, one of which has m. p. 149°.

E. G.

The Nitration of the Chlorotoluenes. ARNOLD F. HOLLEMAN and J. P. WIBAUT (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 594—599).—The position assumed by a third substituent in a benzene ring depends on the relative velocities of substitution caused by the two substituents already present. The hydroxyl, amino-, halogen and methyl groups which cause ortho-para substitution are placed in the order of decreasing velocity.

In order to obtain further knowledge of the relative substitution velocity caused by different groups, the author has re-investigated the nitration products of *o*-chlorotoluene (Goldschmidt and Hönig, A., 1886, 1022). All four possible chloronitrotoluenes, 2 : 3, 2 : 4, 2 : 5, 2 : 6, were found to be present in the product, although the 2 : 4-isomeride proved difficult of detection. For the estimation of the relative amounts of the isomerides in the nitration product, Valeton's modification of the m.-p. method was used, and indicated in a product obtained at 0° from 10 grams of chlorotoluene and 40 grams of nitric acid (D 1·52), 19·2, 17·0, 43·3, and 20·5% respectively, in the above order.

In extending a similar investigation to the nitration of *m*-chlorotoluene, 3 : 6-, 3 : 5-, 3 : 4-, and 3 : 2-chloronitrotoluenes were prepared in a high state of purity, and had m. p. 24·9°, 58·4°, 24·2°, and 23·4° respectively. Analysis of the reaction product indicated no appreciable quantity of the 3 : 5-isomeride, and 58·9, 32·3, and 8·8% of the remaining three.

By a calculation involving the composition of the nitration products of toluene, chlorobenzene and *p*-chlorotoluene, it is deduced that chlorine causes a velocity of substitution 1·491 times as great as that caused by the methyl radicle. The knowledge of this number allows the calculation of the proportion in which the various isomeric products should be formed in the nitration of *o*- and *m*-chlorotoluenes, and the theoretical proportions exhibit a gratifying concordance with the experimental.

D. F. T.

αα-Dihalogenoarylsulphonylacetonitriles, $R \cdot SO_2 \cdot CX_2 \cdot CN$, and a Peculiar Reduction of these Halogen Compounds. JULIUS TRÖGER and W. KROSEBERG (*J. pr. Chem.*, 1913, [ii], **87**, 67—84. Compare A., 1905, i, 336, 870; 1908, i, 633, 798).—It has been shown previously that αα-dibromoarylsulphonylacetonitriles may be

obtained readily by the action of bromine on the sodium salts of arylsulphonyl-α-oximinoacetonitriles, $SO_2R\cdot C(:NOH)\cdot CN$, in aqueous solution. Attempts to prepare the corresponding dichloro- and di-iodo-compounds in a similar manner were unsuccessful. The dichloro-compounds may, however, be obtained by the addition of bleaching powder to a glacial acetic acid solution of the corresponding arylsulphonylacetonitriles, $SO_2R\cdot CH_2\cdot CN$.

The following compounds were prepared in this manner: *αα-dichlorobenzenesulphonylacetonitrile*, $SO_2Ph\cdot CCl_2\cdot CN$, lustrous prisms, m. p. 57°; *αα*-p-*trichlorobenzenesulphonylacetonitrile*, white needles, m. p. 96—97°; *αα-dichloro*-p-*bromobenzenesulphonylacetonitrile*, stout needles, m. p. 105—106°; *αα-dichloro*-p-*iodobenzenesulphonylacetonitrile*, flat prisms, m. p. 111—112°; *αα-dichloro*-p-*toluenesulphonylacetonitrile*, broad, lustrous needles, m. p. 92°; *αα-dichloro*-p-*methoxybenzenesulphonylacetonitrile*, m. p. 121°; *αα-dichloro*-p-*ethoxybenzenesulphonylacetonitrile*, m. p. 95°; *αα-dichloro-ψ-cumenesulphonylacetonitrile*, m. p. 103—104°, and *αα-dichloro-α-naphthalenesulphonylacetonitrile*, m. p. 118°.

The benzenesulphonyl derivative may also be prepared by directly chlorinating benzenesulphonylacetonitrile in glacial acetic acid solution. When dissolved in aqueous sodium hydroxide and the solution treated with a large excess of sodium hypochlorite, benzenesulphonylacetonitrile yields phenyl dichloromethyl sulphone, $CHCl_2\cdot SO_2Ph$.

αα-Dibromo-p-*toluenesulphonylacetonitrile*, prepared from *p*-toluenesulphonylacetonitrile and bromine in glacial acetic acid solution, crystallises in long, white prisms, m. p. 121°; *αα-dibromo*-o-*methoxybenzenesulphonylacetonitrile* forms small prisms, m. p. 123°; *αα-dibromo*-p-*ethoxybenzenesulphonylacetonitrile*, stout, white needles, m. p. 118°; *αα-dibromo-ψ-cumenesulphonylacetonitrile* crystallises in prisms, m. p. 123°; *αα-dibromo-α-naphthalenesulphonylacetonitrile*, in pale yellow needles, m. p. 146°.

Attempts have been made to prepare compounds of the type $SO_2R\cdot CO\cdot CN$: (1) by hydrolysing the α-oximinoarylsulphonylacetonitriles with dilute acids; (2) by the action of silver oxide on the above dihalogen compounds, and (3) by oxidising the arylsulphonylacetonitriles with potassium permanganate, but so far these attempts have not met with success.

When heated with sodium benzenesulphinate in alcoholic solution, αα-dihalogenoarylsulphonylacetonitriles undergo a remarkable reduction to arylsulphonylacetonitriles, thus: $SO_2R\cdot CX_2\cdot CN + 2SO_2PhNa + 2H_2O = 2NaX + 2SO_2Ph\cdot OH + SO_2R\cdot CH_2\cdot CN$.

The action of iodine dissolved in aqueous potassium iodide on the sodium salt of α-oximinobenzenesulphonylacetonitrile leads to the formation of the corresponding *potassium* salt, $SO_2Ph\cdot C(CN):NOK$, which crystallises in lustrous, golden-yellow leaflets.

The authors also record unsuccessful attempts to prepare compounds of the type $SO_2R\cdot C(CN):NO\cdot ONa$ by the condensation of ethyl nitrate and arylsulphonylacetonitriles by means of sodium ethoxide in alcoholic solution; in the case of *p*-chlorobenzenesulphonylacetonitrile, the product of the reaction consisted of the *sodium* salt,

$$C_6H_4Cl\cdot SO_2\cdot CHNa\cdot CN.$$

F. B.

Spontaneous Formation of Iodonium Bases Containing Iodine in a Pentatomic Heterocyclic Nucleus. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 617—620).—When 2:2'-di-iodosodiphenyl, $IO\cdot C_6H_4\cdot C_6H_4\cdot IO$, or 2:2'-di-iododiphenyl tetrachloride, $ICl_2\cdot C_6H_4\cdot C_6H_4\cdot ICl_2$, are kept in water for some months, the aqueous solution yields diphenyleneiodonium iodide, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>I\cdot I$, when treated with sulphur dioxide. In the case of the tetrachloride, the di-iodoso-derivative is probably first formed, together with hydrogen chloride. By subsequent simultaneous oxidation and reduction of the di-iodoso-compound, all the following substances may be produced: $C_6H_4I\cdot C_6H_4I$, $IO_2\cdot C_6H_4\cdot C_6H_4\cdot IO_2$, $C_6H_4I\cdot C_6H_4\cdot IO_2$, $IO\cdot C_6H_4\cdot C_6H_4\cdot IO_2$, and $C_6H_4I\cdot C_6H_4\cdot IO$. By rearrangement of the compound

$$IO\cdot C_6H_4\cdot C_6H_4\cdot IO_2,$$

diphenyleneiodonium iodate, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>I\cdot IO_3$, is produced, and this, by the action of sulphur dioxide, is reduced to the iodide (compare Forster and Schaeppi, T., 1912, 101, 1359). R. V. S.

$\omega\omega'$-Diarylated Aliphatic Hydrocarbons. WALTHER BORSCHE and J. WOLLEMANN (*Ber.*, 1912, 45, 3713—3725. Compare A., 1912, i, 23).—The method for the synthesis of $\alpha\kappa$-diphenyldecane has now been extended to the preparation of other members of the series, with certain modifications in the case of the pentane, heptane, and nonane.

Adipyl chloride, from adipic acid and phosphorus trichloride, condenses with benzene to form $\alpha\zeta$-diphenylhexan-$\alpha\zeta$-dione, m. p. 107° (Etaix, A., 1898, i, 124), *δ-benzoylvaleric acid*, $COPh\cdot[CH_2]_4\cdot CO_2H$, being formed at the same time in white needles, m. p. 70—72°. The diketone has been converted into the dioxime, m. p. 222—223° (*ibid.*), which on reduction yields *$\alpha\zeta$-diamino-$\alpha\zeta$-diphenylhexane*,

$$NH_2\cdot CHPh\cdot[CH_2]_4\cdot CHPh\cdot NH_2,$$

as a colourless oil, b. p. 250—254°/16 mm., the *carbamide* of which, $C_{20}H_{26}O_2N_4$, melts at 121°, and the *benzoyl* derivative, $C_{32}H_{32}O_2N_2$, at 238°. The conversion of the diamine into Rupe and Bürgin's $\alpha\zeta$-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene (A., 1910, i, 161) gives a poor result, but the method of von Braun and Deutsch (A., 1912, i, 687) provides a better way of obtaining the desired $\alpha\zeta$-diphenylhexane.

In the same way, suberyl chloride has been converted into the corresponding dioxime (Etaix, *loc. cit.*), and this has been reduced and the phosphate of the diamine has been distilled. A good yield of *$\alpha\theta$-diphenyl-$\Delta^{\alpha\eta}$-octadiene*, $CHPh:CH\cdot[CH_2]_4\cdot CH:CHPh$, is thus obtained in colourless leaflets, m. p. 61—62°, b. p. 210—220°/11 mm.; it gives a *tetrabromide*, $C_{20}H_{22}Br_4$, m. p. 196°, and absorbs hydrogen in the presence of palladium, yielding $\alpha\theta$-diphenyloctane (compare Braun and Deutsch, *loc. cit.*).

A characteristic derivative of $\alpha\kappa$-diphenyldecane (*loc. cit.*) is the nitration product, *2:4:2':4'-tetranitro-$\alpha\kappa$-diphenyldecane*,

$$C_{10}H_{20}[C_6H_3(NO_2)_2]_2;$$

it forms yellowish-white needles, m. p. 63°.

The acid chlorides for the corresponding pentane, heptane, and nonane are difficult to obtain, and the diamines would probably yield ring compounds. Hence, the necessary ketones have been prepared by the reduction of available unsaturated ketones (compare A., 1912, i, 194) and reduced to alcohols, which, on dehydration with zinc chloride, give the olefines. The reduction of distyryl ketone to di-β-phenylethyl ketone is usually accompanied by by-products, the nature of which seems to depend on the condition of the palladium employed. The substance, $C_{34}H_{34}O_2$, m. p. 126° (*ibid.*), has not since been encountered; instead, the $\alpha\epsilon\zeta\kappa$-tetraphenyldecane-$\theta$-dione, $C_{34}H_{34}O_2$, m. p. 173—174°, of Harries and Gollnitz (A., 1904, i, 427), and, apparently, its unsaturated *ketone*, $C_{34}H_{30}O_2$, a white powder, m. p. 207—208°, which dissolves with a purple colour in concentrated sulphuric acid, have been isolated. The required di-β-phenylethyl ketone can be more conveniently prepared from phenylethyl methyl ketone by saturating its benzylidene compound (Harries and Gollnitz, *loc. cit.*) with hydrogen in presence of palladium. On reduction with sodium and alcohol, *$\alpha\epsilon$-diphenylpentan-γ-ol*, $OH\cdot CH(CH_2\cdot CH_2Ph)_2$, is obtained as a very soluble, crystalline mass, m. p. 47—48°, b. p. 218°/11 mm., which, on distillation with zinc chloride, yields *$\alpha\epsilon$-diphenyl-Δ^{β}-pentene* as a colourless oil, b. p. 184—185°/10 mm. Reduction readily results in the $\alpha\epsilon$-diphenylpentane of Braun and Deutsch (A., 1912, i, 435). The same series of reactions has also been carried out with phenyl δ-phenylbutyl ketone (A., 1912, i, 194), which has been obtained in colourless needles, m. p. 47°. *$\alpha\epsilon$-Diphenylpentan-α-ol*, $OH\cdot CHPh\cdot[CH_2]_3\cdot CH_2Ph$, is a colourless oil, b. p. 217°/12 mm., which gives a poor yield of *$\alpha\epsilon$-diphenyl-Δ^{α}-pentene*, a colourless, mobile liquid, b. p. 186°/11 mm., which polymerises when heated. The $\alpha\epsilon$-diphenylpentane forms a *tetranitro*-derivative, $C_{17}H_{16}O_8N_4$, in slender, yellow needles, m. p. 126°.

$\alpha\eta$-Diphenylheptan-γ-one is best obtained by the reduction of *$\alpha\eta$-diphenyl-Δ^{α}-hepten-γ-one*, $CHPh:CH\cdot CO\cdot[CH_2]_3\cdot CH_2Ph$, which is formed in colourless leaflets, m. p. 25°, b. p. 240°/12 mm., by the condensation of benzaldehyde with methyl-δ-phenylbutyl ketone (A., 1911, i, 880). Its reduction product, *$\alpha\eta$-diphenylheptan-γ-ol*, m. p. 42—43°, b. p. 233°/11 mm., is very readily dehydrated, and the heptene is also easily reduced to *$\alpha\eta$-diphenylheptane*, b. p. 207—208°/12 mm.

In the same way, $\alpha\iota$-diphenylnonan-ϵ-one (A., 1912, i, 194) has been reduced to *$\alpha\iota$-diphenylnonan-ϵ-ol*, a viscous, colourless liquid, b. p. 251°/11 mm., which yields the *$\alpha\iota$-diphenyl-Δ^{ϵ}-nonene* as a highly refractive oil, b. p. 231—233°/12 mm. Reduction of the latter to *$\alpha\iota$-diphenylnonane*, a colourless oil, b. p. 235°/12 mm., proceeds very readily.

J. C. W.

Pyrosulphates of Sodium and Potassium as Condensing Agents. ALLAN F. ODELL and CLEVE W. HINES (*J. Amer. Chem. Soc.*, 1913, 35, 81—84).—The alkali pyrosulphates have been used as condensing agents by Bogojavlenski and Narbutt (A., 1905, i, 854) in the preparation of certain esters. The salts are readily converted into the hydrogen sulphates by the addition of water, and should,

therefore, be efficient agents for the abstraction of water in organic synthesis; they are easily prepared and convenient to handle.

The pyrosulphates have now been applied to the preparation of triphenylbenzene, benzylideneaniline, benzylidenemalonic acid, phenylstyryl ketone and acetanilide, and have given good results. They cannot be employed, however, to effect the condensation of phenols with other substances. E. G.

Nitro-derivatives of *m*-Cresyl Oxide [*m*-Tolyl Ether]. ALPHONSE MAILHE (*Compt. rend.*, 1912, **155**, 1524—1526).—A study of the nitration of *m*-tolyl ether prepared by the aid of thorium oxide (compare A., 1912, i, 767). Nitration in acetic acid solution at the ordinary temperature yields *nitro*-m-*tolyl ether*,

$$C_6H_4Me\cdot O\cdot C_6H_3Me\cdot NO_2,$$

b. p. 245—250°/50 mm., m. p. 48°, which on reduction with iron and acetic acid gives the corresponding *amine*, giving a violet coloration with calcium chloride. If during the nitration the temperature rises to 80—90°, *dinitro*-m-*tolyl ether*, $O(C_6H_3Me\cdot NO_2)_2$, prisms, m. p. 112°, is obtained, in which the nitro-groups are probably para to the oxygen.

By gradually adding tolyl ether to fuming nitric acid, kept cold, and then adding water, a paste is obtained, which, after extraction of the above dinitro-compound, is added to a mixture of sulphuric and nitric acids and yields 2 : 4 : 2′ : 4′-*tetranitro*-m-*tolyl ether*,

$$O[C_6H_2Me(NO_2)_2]_2,$$

a white, amorphous powder, m. p. 203°, which on boiling with concentrated aqueous potassium hydroxide yields *dinitrodihydroxy*-m-*tolyl ether*, a black, crystalline powder, m. p. 300° (decomp.).

If the original tolyl ether is nitrated in sulphuric acid solution by the gradual addition of fuming nitric acid, the temperature being gradually raised to 90° towards the end of the reaction, 2 : 6 : 2′ : 6′-*tetranitro*-m-*tolyl ether*, hexagonal plates, m. p. 147°, is obtained together with a large proportion of its isomeride. Attempts to carry the nitration further have, as yet, not been successful. W. G.

Preparation and Oxidation of Styrolene Alcohol [Phenylethylene Glycol]. WM. LLOYD EVANS and LOU HELEN MORGAN (*J. Amer. Chem. Soc.*, 1913, **35**, 54—68).—This investigation was undertaken with the object of determining the mechanism of the oxidation of phenylethylene glycol (styrolene alcohol) with different reagents, and of establishing the conditions under which mandelaldehyde might be isolated as an intermediate product. Zincke (*Annalen*, 1883, **216**, 303) has shown that on oxidising the glycol with chromic acid, benzaldehyde, formaldehyde, and formic acid are produced, that with potassium permanganate a quantitative yield of benzaldehyde may be obtained, and that with nitric acid, benzoylcarbinol and benzoylformic acid are formed.

Phenylethylene glycol is best prepared by the hydrolysis of the corresponding diacetate (Zincke, *loc. cit.*). On oxidation with potassium permanganate, either alone or in presence of alkali hydroxide, it yields benzoic acid, but not phenylglyoxylic acid, the reaction taking place

in accordance with the equation: (1) $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}OH \longrightarrow C_6H_5{\cdot}CHO + CH_3{\cdot}OH$ or

(2) $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}OH \longrightarrow C_6H_5{\cdot}CH_2{\cdot}OH + {:}CH{\cdot}OH$

When the glycol is oxidised with potassium ferricyanide, benzoic acid is the chief product, but mandelic acid is not formed, and the reaction proceeds according to equation (1) or (2). With silver oxide, in presence of alkali hydroxide, the oxidation takes place, with formation of benzoylcarbinol as the first product of the reaction, in one of the following ways: (3) $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}OH \longrightarrow C_6H_5{\cdot}\overset{|}{\underset{|}{C}}{\cdot}CH_2{\cdot}OH + H_2O$; and $C_6H_5{\cdot}\overset{|}{\underset{|}{C}}{\cdot}CH_2{\cdot}OH + H_2O \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}OH + 2H$; or (4) $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}OH \longrightarrow C_6H_5{\cdot}CH(OH){\cdot}CH{:} + H_2O$, and

$C_6H_5{\cdot}CH(OH){\cdot}CH{:} + H_2O \longrightarrow C_6H_5{\cdot}CH(OH){\cdot}CHO + 2H$;

at 60°, both reactions occur. If silver oxide is employed alone at 20°, the reaction seems to proceed entirely in accordance with equation (3). The oxidation of phenylethylene glycol by bromine in presence of potassium carbonate yields benzoylcarbinol. Aqueous solutions of copper salts do not exert any marked action on the glycol even at 100°. E. G.

Preparation of Benzyl Mercaptan. JOHN A. SMYTHE (*Proc. Univ. Durham, Phil. Soc.*, 1912, 4, 220—222).—Benzyl mercaptan may be prepared from benzyl sulphide by reduction with iron filings in acetic acid solution. When dissolved in glacial acetic acid, and the solution saturated simultaneously with hydrogen chloride and sulphur dioxide, it yields benzyl disulphide and trisulphide in equal amounts. F. B.

Derivatives of Ethylene Dimercaptan, $SH{\cdot}CH_2{\cdot}CH_2{\cdot}SH$, s-Dithiolethylene, $SH{\cdot}CH{:}CH{\cdot}SH$, and of Dithiolacetylene, $SH{\cdot}C{\vdots}C{\cdot}SH$. EMIL FROMM, HANS BENZINGER, and FRITZ SCHÄFER (*Annalen*, 1912, 394, 325—337).—s-*Diethylthiolethylene*,

$SEt{\cdot}CH{:}CH{\cdot}SEt$,

b. p. 170°/13 mm., is obtained by the slow addition of dichloroethylene to ethyl mercaptan and potassium hydroxide in alcohol, the mixture being finally heated on the water-bath. The addition of dichloroethylene to benzyl mercaptan in boiling 7·5% alcoholic potassium hydroxide yields s-*dibenzylthiolethylene*, $C_{16}H_{16}S_2$, m. p. 61°, colourless needles, which decomposes by heating into hydrogen sulphide, toluene, benzyl mercaptan, and stilbene, and forms a *dibromide*, $C_{16}H_{16}Br_2S_2$, m. p. 73—74°, with bromine in carbon disulphide. By heating with alcoholic potassium hydroxide, this dibromide yields *dibenzylthiolacetylene*, $CH_2Ph{\cdot}S{\cdot}C{\vdots}C{\cdot}S{\cdot}CH_2Ph$, m. p. 53°, straw-yellow needles or flesh-coloured leaflets.

s-*Dibenzylthiolethane*, $CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2Ph$, m. p. 38°, prepared from ethylene dibromide and sodium benzyl mercaptide, is oxidised by cold nitric acid (D 1·34) to the *disulphoxide*, $C_{16}H_{18}O_2S_2$, m. p. 198°, white leaflets; the *disulphone*, $C_{16}H_{18}O_4S_2$, pearly leaflets subliming at 304°, is obtained by oxidising the disulphoxide by 5% potassium permanganate, or the sulphide by chromic and acetic acids.

s-*Di-o-nitrophenylthiolethylene*, $C_{14}H_{10}O_4N_2S_2$, m. p. 215°, golden-yellow leaflets, prepared from dichloroethylene, *o*-nitrophenyl mercaptan, and alcoholic potassium hydroxide, forms a *dibromide*,

$$C_{14}H_{10}O_4N_2Br_2S_2,$$

m. p. 132°, citron-yellow prisms, which is converted into *di-o-nitrophenylthiolacetylene*, m. p. 225°, yellow needles, by hot alcoholic potassium hydroxide. This acetylene derivative absorbs only one mol. of bromine in chloroform, forming *dibromodi-o-nitrophenylthiolethylene*, $C_2Br_2(S\cdot C_6H_4\cdot NO_2)_2$, m. p. 209°, yellow leaflets. Sodium *o*-nitrophenyl mercaptide and di-*o*-nitrophenylthiolethylene dibromide react in alcohol to form *glyoxaltetra-o-nitrophenylmercaptal*,

$$CH(S\cdot C_6H_4\cdot NO_2)_2\cdot CH(S\cdot C_6H_4\cdot NO_2)_2,$$

yellow needles, m. p. 178°.

s-*Di-o-aminophenylthiolethylene*, $C_2H_2(S\cdot C_6H_4\cdot NH_2)_2$, m. p. 67°, colourless leaflets, obtained by the reduction of the nitro-compound by alkaline sodium hyposulphite, forms a *dibenzoyl* derivative, m. p. 132°, *diacetyl* derivative, m. p. 159°, and a sparingly soluble *dihydrochloride*, m. p. 201°; the last reacts with only one mol. of sodium nitrite during its diazotisation.

s-*Di-o-nitrophenylthiolethane*, $C_2H_4(S\cdot C_6H_4\cdot NO_2)_2$, m. p. 207°, yellow prisms, prepared by treating moist *o*-nitrophenyl mercaptan and ethylene dibromide with hot alcoholic potassium hydroxide, is oxidised to the *disulphoxide*, $C_{14}H_{12}O_6N_2S_2$, m. p. 145°, pale yellow needles, by chromic and warm glacial acetic acids, and to the *disulphone*, m. p. 164°, almost colourless prisms, by chromic and boiling glacial acetic acids, and yields s-*di-o-aminophenylthiolethane*, m. p. 74° (*dibenzoyl* derivative, m. p. 153°; *diacetyl* derivative, m. p. 194—195°), by reduction with tin and hydrochloric acid.

s-*Di-p-nitrophenylthiolethylene*, m. p. 126°, prepared like the ortho-isomeride, forms a *dibromide*, $C_{14}H_{10}O_4N_2Br_2S_2$, m. p. 137°, yellow needles, and yields by reduction the *diamino*-compound (*diacetyl* derivative, m. p. 194°), which can be readily tetrazotised. s-*Di-p-nitrophenylthiolethane*, m. p. 134°, crystallises in yellow prisms.

Di-2 : 4-dinitrophenyl disulphide, $S_2[C_6H_3(NO_2)_2]_2$, yellow needles, exploding at 280°, is obtained by heating alcoholic 2 : 4-dinitrochlorobenzene with aqueous sodium sulphide and sulphur.

2 : 4-Dinitrophenyl benzyl sulphide yields the *sulphoxide*,

$$C_6H_3(NO_2)_2\cdot SO\cdot CH_2Ph,$$

m. p. 144° (decomp.), straw-yellow needles, by oxidation with 30% hydrogen peroxide in glacial acetic acid, and the *sulphone*, m. p. 177°, by oxidation with chromic and warm glacial acetic acids.

2 : 4-*Dinitrophenyl methyl sulphide*, m. p. 126°, prepared from 2 : 4-dinitrophenyl mercaptan, methyl iodide, and methyl alcoholic sodium methoxide, yields the *sulphoxide*, m. p. 159°, yellow leaflets, and the *sulphone*, m. p. 184° (decomp.), colourless needles, by oxidation with hydrogen peroxide and chromic acid respectively. C. S.

Decomposition of Benzyl Disulphide by Alkalis. EMIL FROMM and AQUILA FORSTER (*Annalen*, 1912, **394**, 338—343).—In addition to the substances identified by Price and Twiss among the products of decomposition of benzyl disulphide by alkalis (T., 1910, **97**,

1175), the authors have detected thiobenzoic acid and dithiobenzoic acid. *Benzyl dithiobenzoate*, $Ph \cdot CS_2 \cdot CH_2Ph$, m. p. 55°, is prepared by heating the acid and benzyl chloride with alcohol and 10% sodium hydroxide.

When the preceding decomposition is effected in the presence of benzyl chloride, the authors could obtain only about 5% of the benzylmercaptal of benzaldehyde instead of 50%, as stated by Price and Twiss (*loc. cit.*), and they suggest that the latters' benzyl chloride was highly contaminated with benzylidene chloride, which reacts with the sodium benzyl mercaptide to form the benzylmercaptal.

[With MAX KLINGER.]—The substance, m. p. 164°, obtained by Fromm and Schmoldt by the dry distillation of benzoyl sulphide, benzoyl disulphide, or thiobenzoic acid, and stated to be tolane tetrasulphide (A., 1907, i, 702), is now shown to be a mixture. By treatment with ammonium sulphide or with ether and petroleum, it is separated into sulphur and tetraphenylthiophen, m. p. 184°. The substance described as tolane disulphide (*loc. cit.*) is probably also a mixture of sulphur and tetraphenylthiophen. C. S.

Some Mercaptals and Mercaptols and their Derivatives. EMIL FROMM, AQUILA FORSTER, and BORIS VON SCHERSCHEWITZKI (*Annalen*, 1912, **394**, 343—349).—The *benzylmercaptal* of formaldehyde, $CH_2(S \cdot CH_2Ph)_2$, m. p. 55°, obtained by saturating with hydrogen chloride a solution of benzyl mercaptan and excess of 40% formaldehyde in glacial acetic acid, is oxidised to the *sulphoxide*, $CH_2(SO \cdot CH_2Ph)$, m. p. 189°, by hydrogen peroxide and to the *sulphone*, $CH_2(SO_2 \cdot CH_2Ph)_2$, m. p. 216°, by acidified 5% potassium permanganate. The *benzylmercaptal* of acetaldehyde,

$$CHMe(S \cdot CH_2Ph)_2,$$

b. p. 200—205°/5 mm., is oxidised to the *sulphone*, $CHMe(SO_2 \cdot CH_2Ph)_2$, m. p. 176°, by 5% potassium permanganate.

The *benzylmercaptole* of acetone, $CMe_2(S \cdot CH_2Ph)_2$, b. p. 195°/5 mm., yields the *sulphoxide*, m. p. 105°, and *sulphone*, m. p. 125°, by oxidation as above. This sulphone and also *αα*-dibenzylsulphone-ethane are produced when dibenzylsulphonemethane is heated with alcoholic methyl iodide and aqueous sodium hydroxide. When *αα*-dibenzylsulphonepropane is similarly treated, benzylmethylsulphone is obtained, owing to the intermediate formation of benzylsulphinic acid. The following substances are also described: the p-*tolylmercaptal* of formaldehyde and its *sulphoxide*, m. p. 45°, and *sulphone*, m. p. 135°; the p-*tolylmercaptole* of acetone, m. p. 64—65°, and its *sulphoxide*, m. p. 75—76°, and *sulphone*, m. p. 147—148°; *αα-di* p-*tolylsulphone-ethane*, m. p. 156°, and *αα-di*-p-*tolylsulphonepropane*, m. p. 189°. C. S.

Catalysis of Dehydrogenation of Hexahydrobenzoic [*cyclo*-Hexanecarboxylic] Acid. NICOLAI D. ZELINSKI and N. UKLONSKAJA (*Ber.*, 1912, **45**, 3677—3678).—An extension of the process which proved successful with *cyclo*hexane and its methyl derivative to simple derivatives which are not hydrocarbons (Zelinski, A., 1911, i, 958).

When *cyclo*hexanecarboxylic acid is added gradually to palladium

black at 300° in an atmosphere of hydrogen at 20—25 mm. pressure, the vapours which pass away on condensation give crystals of benzoic acid in a smaller quantity of unchanged liquid *cyclo*hexanecarboxylic acid.

If ethyl *cyclo*hexanecarboxylate (b. p. 195—197°, n^{17} 1·4424) is submitted twice to the above treatment, the liquid product can be separated by distillation into two fractions, the smaller one consisting of a mixture of ethyl benzoate and ethyl benzoate (n^{18} 1·5071), whilst the main fraction is of pure ethyl *cyclo*hexanecarboxylate. The progress of the dehydrogenation can be conveniently followed by the change in the refractive index.

As with *cyclo*pentane and its methyl derivative, no dehydrogenation was observed when methyl*cyclo*pentanecarboxylic acid was treated in a similar manner. D. F. T.

Study of Double Linkings. ANTONIO MADINAVEITIA and JOSÉ SUREDA BLANES (*Anal. Fis. Quim.*, 1912, 10, 381—389).—Under the influence of platinum black, cinnamic acid in glacial acetic acid solution is fully hydrogenised to Zelinski's *cyclo*hexylpropionic acid, whilst palladium black and colloidal palladium determine reduction to phenylpropionic acid. *Octahydroeugenole*, prepared by the hydrogenation of eugenole with platinum black as catalyst, has b. p. 125° at 12 mm., and forms an oil soluble in acetic acid, alcohol and ether, and insoluble in water and light petroleum. In the presence of palladium black, eugenole is reduced to hydroeugenole. G. D. L.

Some Para-derivatives of Phenylacetic Acid. S. ROBSON (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 225—227).—*p*-Bromophenylacetic acid, m. p. 114—115°, has been prepared from *p*-nitrophenylacetonitrile by reduction with stannous chloride, followed by replacement of the amino-group by bromine by means of the diazo-reaction, and finally hydrolysing the resulting *p*-bromophenylacetonitrile, m. p. 112°, with sulphuric acid; on nitration it yields 4-bromo-3-nitrophenylacetic acid (Bedson, T., 1880, 37, 100).

p-Chloro- and *p*-iodo-phenylacetic acids have been prepared in a similar manner. F. B.

Walden's Inversion and Substitution Processes. II. EMIL FISCHER (*Annalen*, 1912, 394, 350—362. Compare A., 1911, i, 418). —Mainly a reply to Biilmann (A., 1912, i, 420) and to Noyes and Potter (*ibid.*, 786).

Phenylpropiolic acid is reduced to cinnamic acid by zinc dust in alkaline as well as in acid solution (compare A., 1912, i, 187); consequently, the presence of the acid is not the cause of the presumably abnormal course of the reduction. C. S.

Behaviour Towards Light of Cinnamylideneacetonitrile of α-Phenylcinnamylideneacetic Acid, and of the Two Cinnamylideneacetic Acids. HANS STOBBE [and NICOLAUS BARBASCHINOV] (*Ber.*, 1912, 45, 3396—3408).—When the dark yellow

α-phenylcinnamylideneacetonitrile, CHPh:CH·CH:CPh·CN, is exposed to light in benzene or chloroform solution, a resin is formed, together with benzoic acid and a colourless dimeride, $C_{34}H_{26}N_2$, m. p. 197°. It thus behaves very similarly to cinnamylidenemalonic acid (Riiber, A., 1902, i, 617), which is polymerised by light to diphenyltetramethylenediethenyldicarboxylic [diphenyl*cyclo*butyldiacrylic] acid. The dimeride, when cautiously oxidised by potassium permanganate in aqueous alkaline methylacetate solution, is converted into benzoyl cyanide and α-truxillic acid, $CO_2H \cdot CH{<}\begin{matrix}CHPh\\CHPh\end{matrix}{>}CH \cdot CO_2H$. This establishes the dimeride as 1 : 3-*diphenyltetramethylene*-2 : 4-*diethenyl*-β-*phenyl*-β-*cyanide* [1 : 3-*diphenyl*cyclo*butane*-2 : 4-*diatroponitrile*],

$$CN \cdot CPh{:}CH \cdot CH{<}\begin{matrix}CHPh\\CHPh\end{matrix}{>}CH \cdot CH{:}CPh \cdot CN.$$

It combines with bromine to a colourless tetrabromide, indicating the absence of a conjugated double bond system, whereas phenylcinnamylidene acetic acid forms only a colourless dibromide. The polymerisation of the cyanide is accompanied by bleaching, the absorption field of the dimeride being displaced some 800 wave-lengths towards the ultraviolet.

On heating at 200°, the dimeride is depolymerised, yielding simply unimolecular cyanide. This behaviour, which is shared by α-truxillic acid, is not in accordance with that of other *cyclo*butane derivatives, and throws some uncertainty on the four-ring formulæ adopted.

A second colourless dimeride, m. p. 215°, is formed during exposure to light. This is also produced as a by-product of the action of bromine on the first dimeride. It does not unite with bromine, and it is not so easily depolymerised; the constitution has not been determined.

α-Phenylcinnamylideneacetic acid, whether used in the form of the acid, its sodium salt or methyl ester, is stable towards light in the absence of oxygen, but in presence of air it is oxidised to benzaldehyde and benzoic acid. No polymerisation product is formed. The methyl ester is more readily oxidised than the acid, whilst the sodium salt is still more resistant.

Similarly under no conditions could a polymeride be obtained from the isomeric cinnamylideneacetic acids. Some oxidation takes place, also the *allo*-acid is converted into its isomeride.

The dimeric acid, $C_{22}H_{20}O_4$, obtained by Riiber (*loc. cit.*) on heating the dimeride of cinnamylidenemalonic acid could not be depolymerised to cinnamylideneacetic acid. The sodium salt and methyl ester behave similarly to the acid; the ester is more easily oxidised under the influence of light; the salt is more stable than the acid. The different behaviour of the compounds studied is not due to any differences in the selective absorption of light by them.

The *dibromide*, $C_{17}H_{13}NBr_2$, from phenylcinnamylideneacetonitrile, crystallises in colourless needles, m. p. 118°. The *tetrabromide* $C_{34}H_{26}N_2Br_4$, of the dimeride has m. p. 276°.

Cinnamylidenemalonic acid forms a *dibromide*, $C_{12}H_{10}O_4Br_2$, m. p. 180°. The *tetrabromide* of the dimeride has decomp. above 100°.

Methyl allo*cinnamylideneacetate* is an oil, solidifying below −80°.

E. F. A.

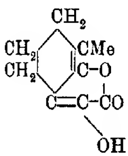
Some Pharmaceutical Incompatibilities of Salol [Phenyl Salicylate]. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 610—616. Compare Caille, A., 1909, i, 594).—In pharmaceutical practice it is not infrequently observed that two dry, solid drugs yield a pasty or liquid mixture. This phenomenon is not due in all cases to the occurrence of a chemical reaction, but results in some cases from the formation of an eutectic mixture of low m. p. In the present paper the author gives tables and curves which exhibit the results of the thermal analysis of the binary mixtures of salol with the substances mentioned in the following list:

	Eutectic.			Eutectic.	
	Temp.	% Salol.		Temp.	% Salol.
β-Naphthol	34°	90	Chloral hydrate ...	17°	61
Antipyrine	30	83	Thymol	13	66
Urethane	29	86	Camphor	6	56
Menthol	28	45	Guaiacol	3	53
β-Bromocamphor.,	21	64			

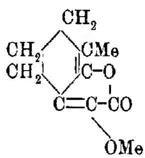
In the system salol-menthol there is complete miscibility in the solid state, the curve being Roozeboom's type III. with a minimum at about 28° and 45% of salol. From the temperature given it follows that some of the above binary mixtures are pasty at ordinary temperatures, others liquid. R. V. S.

Condensation of Cyclic Ketones with Ethyl Oxalate. ARTHUR KÖTZ, K. BLENDERMANN, and J. MEYER (*Ber.*, 1912, 45, 3702—3705. Compare A., 1906, 88, 668).—Active 1-methyl*cyclo*hexan-3-one condenses in the cold with ethyl oxalate and sodium ethoxide, and when the dry product is treated with methyl iodide and subsequently hydrolysed, 1:4-dimethyl*cyclo*hexan-2-one is obtained, b. p. 51°/10 mm. Its *oxime*, $C_8H_{15}ON$, has m. p. 97—98°.

Inactive 1-methyl*cyclo*hexan-2-one condenses to form a *methyl*cyclo*hexenolpyruvolactone*, $C_9H_{10}O_3$, m. p. 141°, alcohol being eliminated. When this is treated with methyl iodide, a *dimethyl compound*, $C_{10}H_{12}O_3$, m. p. 87°, is formed, which absorbs 4 atoms of hydrogen and yields 1-methyl*cyclo*hexan-2-one on hydrolysis. Since these compounds give no reactions for ketones, and since Claisen has shown that the formation of lactones is possible in such circumstances (A., 1895, i, 373), they may be represented by the annexed formulæ.



and



J. C. W.

Melting Point of Ethyl Gallate. HENRY C. BIDDLE (*J. Amer. Chem. Soc.*, 1913, 35, 96).—Biddle and Kelley (A., 1912, i, 714) suggested that the peculiar behaviour of ethyl gallate on melting might be due to the existence of two crystalline forms. It has now been found, however, that by continued purification the ester can

be obtained in long, colourless needles, melting fairly sharply at 160°. E. G.

Kojic Acid, a New Organic Acid Formed by Aspergillus oryzæ. T. YABUTA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, 5, 51—58).—*Kojic acid*, $C_{10}H_8(OH)_4(CO_2H)_2$, obtained from finely powdered *Aspergillus oryzae*, forms colourless needles or prisms, m. p. 152°. The acid gives a strong red colour with ferric chloride; it has no action on alkaline diazobenzenesulphonic acid, on Millon's reagent, or on Fehling's solution. The aqueous solution absorbs much bromine. Methoxyl and ethoxyl groups are not present. The *copper* salt, $C_{12}H_{12}O_8Cu$, forms light green, rhombic crystals. The *acetyl* derivative, $C_{12}H_{10}O_4(OAc)_4$, crystallises from alcohol in colourless needles, m. p. 102°. The *dibenzoyl* derivative, $C_{12}H_{10}O_4(OH)_2(OBz)_2$, m. p. 137°, and the *tetrabenzoyl* derivative, $C_{12}H_{10}O_4(OBz)_4$, m. p. 135°, were prepared.

The acid also occurs in *Aspergillus albus*, *A. candidus*, and *A. nidulans*, but was not found in thirteen other varieties or in *Penicillium* or *Mucor*.

The production of the acid seems to depend on the food supplied to the *Aspergillus*. It was found in *Aspergillus* grown on certain cereals and potatoes, but not with leguminous seeds. N. H. J. M.

Synthesis of β-Glucosidogallic Acid. EMIL FISCHER and HERMANN STRAUSS (*Ber.*, 1912, 45, 3773—3779).—Ethyl gallate combines with acetobromoglucose, forming *ethyl tetra-acetylglucosidogallate*, which is completely hydrolysed by cold barium hydroxide solution to *glucosidogallic acid*, $C_6H_{11}O_5\cdot C_6H_2(OH)_2\cdot CO_2H$. This crystallises in colourless, interlaced needles, m. p. 193° (decomp.), after sintering from 155°, $[\alpha]_D^{20}$ −22°. It is monobasic and is hydrolysed by emulsin into dextrose and gallic acid. With ferric chloride a brownish-red coloration is produced, indicating that the *p*-hydroxyl group of the gallic acid is attached to the sugar residue. It differs from the supposed glucosides of gallic acid described by Gibson (A., 1903, i, 355) and by Feist (A., 1912, i, 566, 888).

Ethyl tetra-acetylglucosidogallate crystallises in colourless needles, m. p. 180—181° (corr.), $[\alpha]_D^{20}$ −10·6°. E. F. A.

Some Reduction Products of Ellagic Acid. MAXIMILIAN NIERENSTEIN and FREDERIC W. RIXON (*Annalen*, 1912, 394, 249—258).—The electrolytic reduction of ellagic acid in a divided cell with mercury cathode and nickel anode yields different products at different temperatures. By reduction in 4*N*-sodium hydroxide at the ordinary temperature, ellagic acid yields chiefly *leucoellagic acid*,

$$C_6H(OH)_2{<}{}^{CH(OH)\cdot O}_{O\cdot CH(OH)}{>}C_6H(OH)_2,$$

m. p. 294—296° (decomp.), small needles. This substance is colourless, does not possess any tinctorial properties, forms a *hexa-acetyl* derivative, m. p. 272—275° (decomp.), and a *hexabenzoyl* derivative, m. p. 300—305° (decomp.), and is reconverted into ellagic acid by oxidation with hydrogen peroxide. By boiling with aqueous potassium hydroxide and carbon tetrachloride, leucoellagic acid is converted into the

potassium salt, long rhombohedra, of the *dicarboxylic acid*,

$$CO_2H\cdot C_6(OH)_2<\begin{matrix}CH(OH)\cdot O\\ O\cdot CH(OH)\end{matrix}>C_6(OH)_2\cdot CO_2H,$$

m. p. 123—124° (decomp.), small needles. A solution of the dicarboxylic acid in ethyl acetate has been separated by strychnine into the two (impure) active acids and the meso-modification. The impure *d-acid* has m. p. 122—124° and $[\alpha]_D^{17}+19\cdot9°$; the impure *l-acid* has m. p. 127—131° and $[\alpha]_D^{17}-2\cdot3°$, and the meso-*acid* has m. p. 143—146° (decomp.).

The electrolytic reduction of ellagic acid in alkaline solution at 70° yields pentahydroxydiphenylmethylolide (A., 1908, i, 548), whilst its reduction in concentrated sodium hydroxide at 110° yields 2 : 3 : 4 : 2′ : 3′ : 4′-hexahydroxydiphenyl. C. S.

New Basic Component of the Muscle of the Dog and Its Relation to Hexamethylornithine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1912, **59**, 433—440).—*Myokynine*, a basic substance obtained from dog's muscle, is probably *l*-hexamethylornithine. Both substances give precipitates with phosphotungstic acid and with alcoholic mercuric chloride solution.

The *aurichloride* from myokynine contains $2H_2O$ and is lævorotatory, that from *hexamethylornithine*, m. p. 204—205°, is anhydrous. Myokynine *platinichloride* ($2H_2O$) has m. p. 232—234°; the isomeride (H_2O) has m. p. 232—233°.

Hexamethylornithine is obtained from ornithine by means of methyl sulphate; it is dextrorotatory. E. F. A.

The Bromination of *cyclo*Pentanone. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1912, **155**, 1522—1524).—When bromine (4 mols.) dissolved in carbon tetrachloride is added to a solution of *cyclo*pentanone (1 mol.) in the same solvent, either with or without the presence of aluminium bromide, the mixture being kept cold, there is obtained, on evaporating off the solvent, an abundant crop of crystals with more or less oil. The crystals are separated, and on purification yield *tetrabromo*cyclo*pentanone*, $C_5H_4OBr_4$, large plates, m. p. 99°. It is very soluble in ether, ethyl acetate, etc., and when left to itself slowly loses hydrogen bromide and is converted into a yellow oil. This change takes place rapidly in solution in ethyl acetate, and the product when purified is *tribromo*cyclo*pentenone*, $C_5H_3OBr_3$, colourless prisms, m. p. 57—58°. This substance on bromination in carbon tetrachloride solution adds on two atoms of bromine, giving *pentabromo*cyclo*pentanone*, $C_5H_3OBr_5$, m. p. 93°.

The oil obtained in the original bromination slowly loses hydrogen bromide, and on boiling the product with water and extracting with ether, a *compound* is obtained, m. p. 147°, which analysis shows to be either $C_5H_8O_2Br$ or $C_5H_5O_2Br$, the amount of material to hand not allowing of definite distinction between the two formulæ. The substance functions both as an alcohol and a ketone. W. G.

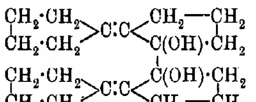
2 : 2-Dimethyl*cyclo*heptanone. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1913, **156**, 75—77).—The dehydration of *cyclo*hexanoldimethylcarbinol gives rise to a hydrocarbon, C_8H_{14}, and two isomeric ketones,

$C_9H_{16}O$, one of which has been shown to be 1-acetyl-1-methyl*cyclo*hexane (compare A., 1910, i, 557), and the other is now proved to be 2 : 2-*dimethyl*cyclo*heptanone*, $Me_2C{<}\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CO-CH_2-CH_2\end{matrix}$, the :CO group having been introduced into the hexatomic ring. By purification through its oxime, it is obtained as a colourless liquid, b. p. 82°/18 mm., giving a *carbanilino-oxime*, m. p. 94°, and a *semicarbazone*, m. p. 176°. On oxidation with weak alkaline permanganate, it yields *a-keto-ββ-dimethylpimelic acid*, $CO_2H\cdot CO\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 67°, giving a *semicarbazone*, m. p. 185°, and an *oxime*, m. p. 140—141°, which on heating further decomposes, losing carbon dioxide and water, giving *δ-cyano-δδ-dimethylpentoic acid*,

$$CN\cdot CMe_2\cdot[CH_2]_3\cdot CO_2H,$$

m. p. 34—35°, which on hydrolysis with alcoholic potassium hydroxide is converted into *aa*-dimethyladipic acid. W. G.

Electrolysis of *cyclo*Pentanone. Marcel Godchot and Félix Taboury (*Bull. Soc. chim.*, 1913, [iv], 13, 12—17. Compare A., 1912, i, 34, 552).—On electrolysis in alkaline solution, *cyclo*pentanone yields *cyclo*pentylidene*cyclo*pentanone (Wallach, A., 1897, i, 160) and two other products, which appear to be tetra*cyclo*pentane derivatives. It is probable that the *cyclo*pentylidene*cyclo*pentanone is formed by the condensation of two mols. of *cyclo*pentanone in presence of alkali, and that the other two products are formed from the condensation product by electrolytic action, the first being the corresponding pinacone and the second the corresponding pinacolin. These supposed tetra*cyclo*pentane derivatives have the following characters. The first, m. p. 160—162°, has the formula $C_{20}H_{30}O_2$, and is probably identical with the substance obtained by Meiser (A., 1899, i, 741). It probably has the annexed constitution, which makes it the pinacone corresponding with *cyclo*pentylidene*cyclo*pentanone.



This substance probably loses 1 mol. of water, giving rise to the second *product*, $C_{20}H_{28}O$, b. p. 320°/25 mm., a yellow liquid which gives no typical carbonyl derivatives, although it probably has the following constitution, being formed in a manner analogous to the transformation of the pinacone of *cyclo*pentanone into the corresponding pinacolin (Meiser, *loc. cit.*), $\begin{matrix}CH_2-CH_2\\ CH_2\cdot C(C_5H_8)\end{matrix}{>}C{<}\begin{matrix}CH_2-CH_2\\ CO\cdot C(C_5H_8)\end{matrix}{>}CH_2$.

T. A. H.

Terpenes and Ethereal Oils. CXII. Condensation Products of Cyclic Ketones and Acetone. Otto Wallach and Wolfgang von Rechenberg (*Annalen*, 1912, 394, 362—384).—Many years ago a substance, $C_{10}H_{16}O$, isomeric with pulegone, was obtained by the condensation of acetone and methyl*cyclo*hexan-3-one, but its constitution could not be definitely settled (A., 1896, i, 310; 1898, i, 484). An extensive examination of similar condensations now leads to the generalisation that the acetone attacks the carbonyl group of *cyclo*hexanones, but a nuclear methylene group of *cyclo*-

pentanones; thus equal molecular quantities of *cyclo*pentanone and acetone are kept in alcoholic sodium ethoxide for some hours at 0°, and then for two to three days at the ordinary temperature, whereby, in addition to a little mesityl oxide, *propylidene*cyclo*pentan-2-one*,

$$CMe_2{:}C{<}\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix},$$

b. p. 195—199°, D^{20} 0·9565, n_D^{20} 1·4932, is obtained (*semicarbazone*, m. p. 215—218°; *oxime*, m. p. 77°), by the reduction of which by hydrogen and colloidal palladium, iso*propyl*cyclo*pentan-2-one*, b. p. 176·5—177·5°, D^{21} 0·9000, n_D^{21} 1·4419 (*semicarbazone*, m. p. 197°; *benzylidene* derivative, m. p. 79—80°), is formed. In a similar manner, i-*methyl*cyclo*pentan-3-one*, b. p. 144—144·5°, D^{22} 0·913, n_D 1·4329 (*semicarbazone*, m. p. 185°; *benzylidene* derivative, m. p. 157°; m-*nitrobenzylidene* derivative, m. p. 174°; *anisylidene* derivative, m. p. 197—198°; *piperonylidene* derivative, m. p. 166—167°; *cinnamylidene* derivative, m. p. 148° [compare A., 1904, i, 752; 1908, i, 424]), prepared from *i*-β-methyladipic acid, condenses with acetone to form 1-*methyl-4-propylidene*cyclo*pentan-3-one*, $CMe_2{:}C{<}\begin{matrix}CH_2\cdot CHMe\\ CO-CH_2\end{matrix}$, b. p. 203—205°, D^{21} 0·9315, n_D^{21} 1·4846 (*semicarbazone*, m. p. 210°; *oxime*, m. p. 89°). The constitution of this compound is determined by its exalted molecular refraction, and by the fact that 1-*methyl*-4-iso*propyl*-cyclo*pentan-3-one*, b. p. 186—187°, D^{20} 0·8850, n_D^{20} 1·4392 (*semicarbazone*, m. p. 179°; *oxime*, m. p. 66°), obtained from it by Paal's method, yields by oxidation with chromic and dilute sulphuric acids a *keto-acid*, $CHMe_2\cdot CO\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$ (*semicarbazone*, m. p. 164°; *oxime*, m. p. 76—77°), by the further oxidation of which *i*-β-methylglutaric acid is produced.

*cyclo*Hexanone and acetone condense to form Δ^1-cyclo*hexenylacetone*, $C_6H_9\cdot CH_2\cdot COMe$, b. p. 203—204°, D^{19} 0·9375, n_D 1·4736 (*semicarbazone*, m. p. 144—145°; *oxime*, b. p. 135°/20 mm.), the constitution of which follows from its molecular refraction and from its reduction by Paal's method to *cyclo*hexylacetone, m. p. 171—172° (not 165—166°, A., 1907, i, 616). cyclo*Hexyltrimethylcarbinol*, $C_6H_{11}\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 208°, D^{20} 0·902, n_D^{20} 1·4627, is prepared from *cyclo*hexylacetone and magnesium methyl iodide in the usual manner.

Methyl*cyclo*hexan-4-one and acetone yield 1-*methyl*-Δ^3-cyclo*hexenyl-4-acetone*, $C_6H_8Me\cdot CH_2\cdot COMe$, b. p. 216—217°, D^{21} 0·916, n_D^{21} 1·4672 (*semicarbazone*, m. p. 122—123°), by the reduction of which 1-*methyl*-cyclo*hexyl-4-acetone*, b. p. 214—215°, D^{21} 0·8930, n_D^{21} 1·4499 (*semicarbazone*, m. p. 166°), is formed.

The compound $C_{10}H_{16}O$, obtained from active methyl*cyclo*hexan-3-one and acetone (*loc. cit.*), is now proved to be 1-*methyl*-$\Delta^{2(or\ 3)}$-cyclo*hexenyl-3-acetone*, $C_6H_8Me\cdot CH_2\cdot COMe$, or a mixture of both. By reduction by Paal's method, it yields 1-*methyl*cyclo*hexyl-3-acetone*, $C_6H_{10}Me\cdot CH_2\cdot COMe$, b. p. 212—214°, $D^{21\cdot5}$ 0·8915, $n_D^{21\cdot5}$ 1·4496 (*semicarbazone*, m. p. 154°), which is converted by alkaline hypobromite into 1-methyl*cyclo*hexyl-3-acetic acid, and by magnesium methyl iodide ultimately into 1-*methyl*cyclo*hexyltrimethylcarbinol*,

$$C_6H_{10}Me\cdot CH_2\cdot CMe_2\cdot OH,$$

b. p. 117°/20 mm. (*phenylurethane*, m. p. 126°). By the elimination of water, the carbinol yields a *hydrocarbon*, $C_{11}H_{20}$, b. p. 186·5—187·5°, D^{20} 0·8120, n_D^{20} 1·4546. *i*-Methyl*cyclo*hexan-3-one condenses with acetone in the same manner as the active substance, yielding a *compound*, $C_{10}H_{16}O$, b. p. 214—217°, D^{21} 0·918, n_D 1·4704 (*semicarbazone*, m. p. 150—151°).

1-Methyl*cyclo*hexan-2-one and acetone, after keeping with alcoholic sodium ethoxide for four weeks, yield mesityl oxide and 1-*methyl*-Δ^1-cyclo*hexenyl-2-acetone*, b. p. 216—217°, D^{19} 0·936, n_D^{19} 1·4778 (*semicarbazone*, m. p. 173—174°); the latter yields by reduction by Paal's method, 1-*methyl*cyclo*hexyl*-2-*acetone*, b. p. 212—214°, D^{21} 0·9050, n_D^{21} 1·4546 (*semicarbazone*, m. p. 179°), from which 1-*methyl*cyclo*hexyl*-2-*acetic acid* (*silver* salt, $C_9H_{15}O_2Ag$; *amide*, m. p. 160—161°) is obtained by oxidation by alkaline hypobromite. C. S.

Studies in the *cyclo*Pentadiene Series. II. 5-Nitro-2:3-dibenzoyl*cyclo*pentadiene. WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc.*, 1913, 35, 68—75).—It has been shown by Hale (A., 1912, i, 566) that acetonylacetone condenses with nitromalonaldehyde to form 5-nitro-2 : 3-diacetyl*cyclo*pentadiene. A similar condensation has now been effected with diphenacyl.

When diphenacyl (1 mol.) is added to a solution of sodium nitromalonaldehyde (1 mol.) and sodium hydroxide (2 mols.), and the mixture is left for eight to ten days at 40°, 5-*nitro*-2 : 3-*dibenzoyl*cyclo-*pentadiene*, $NO_2\cdot CH<\begin{matrix}CH:CBz\\ |\\ CH:CBz\end{matrix}$, m. p. 237—238° (decomp.), is obtained in a yield of 75% of that calculated from the amount of aldehyde used. The compound crystallises in yellow prisms; its *sodium*, *barium*, and *silver* salts are described. The *oxime*, m. p. 155—156° (decomp.), and the *anil*, m. p. 264—265°, form slender, yellow needles. The *phenylhydrazone* crystallises in yellow needles; it is unstable and readily undergoes an intramolecular condensation.

If 5-nitro-2 : 3-dibenzoyl*cyclo*pentadiene is boiled with dilute nitric acid, it undergoes oxidation with production of carbon dioxide, oxalic acid, and benzoic acid. A similar result is obtained by means of an alkaline solution of potassium permanganate, 1 mol. of the compound yielding carbon dioxide (3 mols.), oxalic acid (1 mol.), nitric acid (1 mol.), and benzoic acid (2 mols.). E. G.

Thio-derivatives of Ketones. EMIL FROMM (*Annalen*, 1912, 394, 290—309).—[With FRITZ HAAS.]—The substance previously described as duplobenzylidenethioacetone by Fromm and Höller (A., 1907, i, 710) is now shown to be a mixture of stereoisomeric bases, the *duplobenzylidenethioacetoneamines*, $C_{20}H_{23}NS_2$, and its extraordinary additive compounds with acids are simply salts of these bases; consequently, the theories advanced by Fromm and Höller to explain the formation of these additive compounds are abandoned. The *hydrochloride*, $C_{20}H_{23}NS_2,HCl$, has m. p. 238°, the *sulphate* has m. p. 192°, and the *nitrate* has m. p. 211°. The substance previously described as duplobenzylidenethioacetone hydrate, and the two additive compounds

with ammonia, m. p. 142° and 148° respectively, are simply duplobenzylidenethioacetoneamine.

The neutral by-product, duplobenzylideneoxythioacetone, m. p. 186°, obtained by Fromm and Höller in the preparation of their so-called duplobenzylidenethioacetone (*loc. cit.*), becomes the main product when sodium sulphide is employed instead of ammonium sulphide. It is now shown to be ***duplobenzylideneacetone sulphide***, $C_{20}H_{22}O_2S$. It forms a *dibromo*-derivative, $C_{20}H_{20}O_2SBr_2$, m. p. 164°, rhombic leaflets, with bromine in chloroform, and is oxidised by 5% potassium permanganate, by fuming nitric acid, or by 30% hydrogen peroxide in glacial acetic acid, to ***duplobenzylideneacetone sulphoxide***, $C_{20}H_{22}O_3S$, m. p. 308°, prisms, which forms a *dibromo*-derivative, $C_{20}H_{20}O_3SBr_2$, m. p. 214°, felted needles, with bromine. By treating a not too concentrated solution of styryl methyl ketone in alcohol with ammonium polysulphide, ***duplobenzylideneacetone disulphide***, $C_{20}H_{22}O_2S_2$, m. p. 125°, is obtained.

Since duplobenzylidenethioacetoneamine yields hydrogen sulphide, ammonia, and styryl methyl ketone-phenylhydrazone by treatment with phenylhydrazine at a temperature not exceeding 140—150°, it probably has the formula $NH[CMe(SH)\cdot CH\colon CHPh]_2$, despite its insolubility in alkalis. Moreover, since it yields duplobenzylideneacetone disulphide by oxidation by hydrogen peroxide or by iodine, the disulphide probably has the formula $S_2[CMe(OH)\cdot CH\colon CHPh]_2$. By moistening with a little alcohol and then shaking with dilute sodium hydroxide, the disulphide is converted into the sulphide. The latter, therefore, is probably $S[CMe(OH)\cdot CH\colon CHPh]_2$, and the sulphoxide is $SO[CMe(OH)\cdot CH\colon CHPh]_2$. The disulphide and the sulphide cannot be benzoylated or acetylated, but both, and also the sulphoxide, yield styryl methyl ketone-phenylhydrazone by treatment with phenylhydrazine.

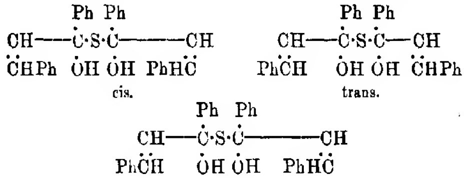
[With Emil Hubert.]—*Benzylideneacetophenone hydrosulphide*, $CHPh\colon CH\cdot CPh(OH)\cdot SH$, m. p. 107°, is obtained by the action at 0° of hydrogen sulphide on an alcoholic solution of phenyl styryl ketone containing a little potassium hydroxide. It forms a *S-benzoyl* derivative, $CHPh\colon CH\cdot CPh(OH)\cdot SBz$, m. p. 125°, which is not oxidised to a disulphide by iodine. *Dibenzylideneacetophenone disulphide*,

$$S_2[CPh(OH)\cdot CH\colon CHPh]_2,$$

m. p. 159°, is obtained by oxidising the preceding hydrosulphide by iodine in alcohol-chloroform solution, or by adding cold alcoholic phenyl styryl ketone to alcoholic sodium sulphide saturated with sulphur and with hydrogen sulphide.

The amorphous α- and β-duplobenzylideneacetophenone sulphides, m. p. 96° and 181° respectively, described by Fromm and Lambrecht (A., 1908, i, 989), are not pure. The pure substances are crystalline, have m. p. 109° and 186° respectively, and have the formula $C_{30}H_{26}O_2S$, not $C_{30}H_{24}OS$. The views previously advanced to explain their isomerism are withdrawn. The pure substances are obtained by the action of alcoholic ammonia on phenyl styryl ketone hydrosulphide in chloroform, an excess of ammonia producing the β-isomeride, m. p. 186°, a little ammonia forming the α-isomeride, m. p. 109°. This method of formation, together with the fact that the two sulphides

yield hydrogen sulphide and 1 : 3 : 5-triphenylpyrazolone by boiling with phenylhydrazine in glacial acetic acid, leads to the formula S[CPh(OH)·CH:CHPh]$_2$ for the two isomerides. α-Duplobenzylideneacetophenone sulphide is converted into the β-isomeride, not by iodine as stated by Fromm and Lambrecht (*loc. cit.*), but by ammonia. The stereoisomerism of the two substances is probably similar to that of dioximes, consequently *cis*-, *trans*-, and *amphi*-modifications



cis. trans. amphi.

should exist. This view of the stereoisomerism receives strong support by the discovery of the third modification required by the theory. α-Duplobenzylideneacetophenone sulphide, m. p. 109° (sulphone, m. p. 198°), is obtained by passing hydrogen sulphide, without cooling, into an alcoholic solution of phenyl styryl ketone containing a little potassium hydroxide. β-Duplobenzylideneacetophenone sulphide, m. p. 186° (sulphone, m. p. 216°), is prepared by saturating an alcoholic solution of phenyl styryl ketone with ammonia and then with hydrogen sulphide. γ-*Duplobenzylideneacetophenone sulphide*, m. p. 212° (*sulphone*, $C_{30}H_{26}O_4S$, m. p. 276°), is obtained by adding an alcoholic solution of phenyl styryl ketone to alcohol saturated with anhydrous sodium sulphide and with sulphur. C. S.

Stereoisomerism of Derivatives of Phenacyl Sulphide. EMIL FROMM and JULIUS FLASCHEN (*Annalen*, 1912, **394**, 310—324).—Phenacyl sulphide is obtained in almost quantitative yield by Tafel and Mauritz's method (A., 1891, 302) when the solution is kept at 0° during the reaction. In addition to the diphenylhydrazone described by these authors, a *phenylhydrazone*, $C_{22}H_{20}ON_2S$, m. p. 126°, yellow needles, can be prepared. Phenacyl sulphide in glacial acetic acid is oxidised to *diphenacyl sulphoxide*, SO(CH$_2$·COPh)$_2$, m. p. 98°, and in benzene is oxidised by a faintly acidified solution of potassium permanganate to *diphenacylsulphone*, m. p. 120°, colourless prisms. The sulphone yields *diphenacylsulphone dibenzylmercaptole*, SO$_2$[CH$_2$·CPh(S·C$_7$H$_7$)$_2$]$_2$, m. p. 110°, by treatment with an excess of benzyl mercaptan in glacial acetic acid saturated with hydrogen chloride, and forms only a *dimethyl* derivative, SO$_2$(CHMe·COPh)$_2$, m. p. 178°, with methyl iodide and sodium ethoxide in alcohol. In boiling glacial acetic acid, phenacylsulphone and the calculated quantity of phenylhydrazine yield *diphenacylsulphonediphenylhydrazone*,

SO$_2$(CH$_2$·CPh:N·NHPh)$_2$.

This crystallises from glacial acetic acid in yellow needles, m. p. 148°, and from alcohol or from benzene and petroleum in pale yellow needles, m. p. 160°. This second modification, which can also be obtained by

the interaction of diphenacylsulphone and phenylhydrazine in alcohol containing a little sodium hydroxide, is converted into the first modification, m. p. 148°, by crystallisation from glacial acetic acid. A third *isomeride*, m. p. 170°, is obtained from diphenacylsulphone and phenylhydrazine in alcohol, *anhydrodiphenacylsulphonephenylhydrazone*,

$$C_{22}H_{18}O_2N_2S,$$

m. p. 187°, being also produced. *Diphenacylsulphonephenylhydrazone*, m. p. 193°, yellow needles, is prepared by crystallising the preceding anhydride from glacial acetic acid or by boiling equal molecular quantities of diphenacylsulphone and phenylhydrazine in the same solvent. Reasons are given for regarding this phenylhydrazone as *trans*-diphenacylsulphonephenylhydrazone and the anhydride as a derivative of the *cis*-isomeride; the diphenylhydrazones, m. p. 148°, 160°, and 170°, are regarded as having the *trans*-, *amphi*-, and *cis*-configurations respectively.

Anhydrodiphenacylsulphonedioxime,

$$\begin{array}{l} CPh\cdot CH \\ \| \\ N\text{——}O \end{array}\!\!>SO\cdot CH_2\cdot CPh\!:\!NOH,$$

m. p. 167° white needles, prepared from diphenacylsulphone and hydroxylamine hydrochloride (2 mols.) in alcohol in the presence of sodium carbonate or acetate, yields *acetyldiphenacylsulphoneoxime*, $C_{18}H_{17}O_5NS$, m. p. 110°, by boiling with acetic anhydride. cis-*Diphenacylsulphonedioxime*, m. p. 204° (*acetyl* derivative, m. p. 158°), is obtained from diphenacylsulphone and an excess of hydroxylamine hydrochloride in boiling alcohol containing a drop of hydrochloric acid. trans-*Diphenacylsulphonedioxime*, m. p. 190° (*acetyl* derivative, m. p. 146°), is obtained together with the monoxime, m. p. 173°, by heating diphenacyl sulphone with hydroxylamine hydrochloride (2 mols.) and calcium carbonate (1 mol.) in alcohol through which carbon dioxide is being passed. cis-*Diphenacylsulphoneoxime*, $C_{16}H_{15}O_4NS$, m. p. 144°, is obtained from equal molecular quantities of diphenacylsulphone and hydroxylamine hydrochloride in the presence of sodium carbonate or acetate. trans-*Diphenacylsulphoneoxime*, m. p. 173°, is obtained from equal molecular quantities of diphenacylsulphone and hydroxylamine hydrochloride in boiling alcohol in the presence of calcium carbonate. The monoximes each yield the same acetyl derivative, m. p. 110°, as that obtained from anhydrodiphenacylsulphonedioxime. The *cis*-oxime, m. p. 144°, yields anhydrodiphenacylsulphonedioxime by further treatment with hydroxylamine hydrochloride and sodium carbonate, and the *cis*-dioxime by treatment with hydroxylamine hydrochloride and calcium carbonate. The *trans*-oxime, m. p. 173°, yields only anhydrodiphenacylsulphonedioxime by treatment with hydroxylamine hydrochloride and sodium carbonate or calcium carbonate. Since the anhydrodioxime is produced from each of the monoximes, it is certainly derived from the *amphi*-dioxime. The configurations of the other substances are not established with certainty, C. S.

Transformations of Thujane. II. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1759—1762. Compare A., 1911, i, 71, 996).—Decomposition by means of aniline or alcoholic potassium hydroxide of the unstable bromide obtained by shaking thujane with

fuming hydrobromic acid for a comparatively short time (two to three hours) yields a mixture of two isomeric hydrocarbons, $C_{10}H_{18}$, the one with the higher boiling point predominating when alkali is employed. The properties of various preparations of these hydrocarbons are as follows: (1) b. p. 160—161·5°/753 mm., D_0^{20} 0·8085 (or 0·8082), n_D 1·4490, $[\alpha]_D$ +17·86° (or +15·59°); (2) b. p. 166—168°/754 mm., D_0^{20} 0·8159 (or 0·8188), n_D 1·4538, $[\alpha]_D$ +6·13° (or +2·8°). If the action of the hydrobromic acid on thujane is prolonged for fifteen hours, distillation of the bromide yielded with aniline gives hydrocarbons with the constants: (1) b. p. 160—162°/762 mm., D_0^{20} 0·8093, n_D 1·4494, $[\alpha]_D$ +3·67°; (2) b. p. 167·5—170°/761 mm., D_0^{20} 0·8171, n_D 1·4555, $[\alpha]_D$ +2·4°.

Both hydrocarbons contain the same carbon-atom nucleus, since reduction of them by Sabatier's method leads to one and the same hydrocarbon, $C_{10}H_{20}$, b. p. 161—163°/753 mm. (or 759 mm.), D_0^{20} 0·7904 (or 0·7902), n_D 1·4319 (or 1·4336), $[\alpha]_D$ −1·29° (or −1·21°)

T. H. P.

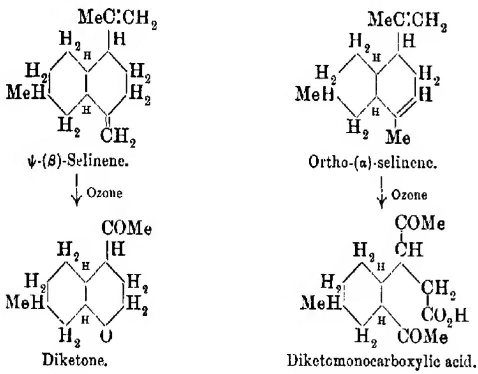
A Special Case of Racemism. MAURIZIO PADOA and G. ROTONDI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 626—631).—The paper deals with the thermal analysis of the system formed by the two modifications (namely, the stable, m. p. 75°, and the labile, m. p. 45°) of optically active bromocamphor (*d*- or *l*-). This presents a case not considered by Roozeboom in his analysis of the criteria for the characterisation of inactive mixtures, because each enantiomorph exists in two modifications. Mixtures containing more than about 58% of *d*-bromocamphor, or more than 58% of *l*-bromocamphor, have an initial m. p., with separation of pure solvent. As the cooling is continued the composition mentioned is reached and the labile form then appears. At this point the whole mass solidifies and pure solvent separates along a curve shown until the inactive conglomerate is reached, which possesses the lowest transformation point. Below the curve just mentioned and the m.-p. curve of the labile modification, only conglomerates of the two bromocamphors are stable. Fused mixtures which contain less than 58% of *d*-bromocamphor and less than 58% of *l*-bromocamphor crystallise in the labile form, and when cooling is continued they are transformed into conglomerates. The labile forms have therefore a small area of stability, bounded by the curve of the labile modification and the curve of the separation of conglomerates already mentioned.

As regards the characterisation of the racemism, the racemic compound exists between 44° and 50·5°; below that it is split into inactive conglomerates. This is analogous to the behaviour of sodium ammonium racemate studied by van't Hoff. R. V. S.

The Constituents of Essential Oils (The Constitution of Selinene). FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, 45, 3725—3731. Compare this vol., i, 66).—In the former communication, the sesquiterpene, selinene, was shown to give a dihydrochloride from which a regenerated selinene with slightly higher rotation, due perhaps to a different arrangement of the unsaturated linkings, could be obtained. In order to elucidate the constitution of these isomerides, they have been oxidised with ozone.

Natural ψ-(β)-selinene on oxidation gave a very small amount of an acid, but chiefly an indifferent product which was purified by conversion into a *disemicarbazone*, $C_{13}H_{20}(N{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, m. p. 228°, from which the saturated *diketone*, $C_{13}H_{20}O_2$, b. p. 178—180°/11 mm., D^{20} 1·0566, n_D 1·49994, $\alpha_D+15°$, was recovered by means of oxalic acid. The fact that two carbon atoms have been eliminated by this process, whereas the acid resulting from the oxidation by hypobromite contains only one carbon atom less, indicates the presence in selinene of one methylene group attached directly to the ring and another in a side-chain.

Regenerated selinene, *ortho*-(α)-selinene, b. p. 128—132°/11 mm., D^{20} 0·9190, n_D 1·50920, $\alpha_D+61°36'$, gives much less of the diketone on treatment with ozone, the chief product being the acid, which has been characterised as *methyl selinenediketomonocarboxylate*, $C_{15}H_{24}O_4$, b. p. 185—190°/11 mm., D^{20} 1·0635, n_D 1·47889, $\alpha_D+4°24'$. The formation of this acid is explained by assuming that the elimination of hydrogen chloride from the dichloride has resulted in the displacement of a double bond into the ring. A consideration of other sesqui-terpenes leads to the adoption of the annexed formulæ.



J. C. W.

Chemical Investigation of the Oil of Chenopodium. II. E. K. Nelson (*J. Amer. Chem. Soc.*, 1913, **35**, 84—90. Compare A., 1911, i, 797).—It has been found that when the glycol anhydride formed by the molecular rearrangement of ascaridole is treated with dilute sulphuric acid, ascaridole α-glycol is produced together with two other crystalline substances, one of which, termed *ascaridole β-glycol*, $C_{10}H_{18}O_3$, crystallises with $1H_2O$; the anhydrous substance has m. p. 103—105°; when this glycol is warmed with dilute sulphuric acid, thymol is produced. The other *substance*, termed the "erythrite," $C_{10}H_{20}O_4$, also crystallises with $1H_2O$, and when anhydrous has m. p. 128—130°; it is decomposed by boiling dilute sulphuric acid with formation of a *ketone*, with a strong menthone-like odour, and a

phenolic substance, m. p. 80—81°; the *semicarbazone* of the ketone has m. p. 182—184°. On oxidising the "erythrite" with alkaline potassium permanganate, an *acid*, $C_{10}H_{18}O_6$, m. p. 190—191°, is produced, which forms rhombic prisms; when this acid is heated at 210°, it is converted into its anhydride, and on further heating yields ascaridic anhydride, m. p. 70—71°. If the acid $C_{10}H_{18}O_6$ is oxidised with potassium permanganate in presence of sulphuric acid, it yields β-methylheptane-$\gamma\zeta$-dione, and it is therefore probable that it is a modification of $\alpha\alpha$-dihydroxy-α-methyl-α-*iso*propyladipic acid. The "erythrite" therefore probably has the structure

$$OH{\cdot}CMe{<}\begin{matrix}CH_2\text{———}CH_2\\ CH(OH){\cdot}CH(OH)\end{matrix}{>}C(C_3H_7){\cdot}OH.$$

The acid, $C_{10}H_{16}O_5$, obtained by the oxidation of the α-glycol, is converted by further oxidation into β-methylheptane-$\gamma\zeta$-dione. When the glycol anhydride is boiled with a saturated solution of oxalic acid, a small quantity of the phenolic substance, m. p. 80—81°, is produced, which is formed on boiling the "erythrite" with dilute sulphuric acid and is also obtained by treating the α-glycol with strong dehydrating agents. On heating the glycol anhydride with benzoic anhydride at 150°, an ester of carvacrol is produced.

From the results of this work, it is considered that the α-glycol has the constitution $CMe{<}\begin{matrix}CH_2\text{———}CH_2\\ \text{-----}O\text{———}\\ CH(OH){\cdot}CH(OH)\end{matrix}{>}C{\cdot}C_3H_7$, and that the acid obtained by its oxidation has the structure of $\alpha\delta$-cineolic acid, $CO_2H{\cdot}\underbrace{CMe{\cdot}CH_2{\cdot}CH_2{\cdot}C}_{O}(C_3H_7){\cdot}CO_2H$. E. G.

Action of Gaseous Oxygen on Caoutchouc. STANLEY J. PEACHEY (*J. Soc. Chem. Ind.*, 1912, 31, 1103—1104).—When purified caoutchouc, in the form of a thin film, is exposed to an atmosphere of oxygen at a temperature of 85°, oxidation commences after a few hours' heating, and then proceeds rapidly to completion. Results of experiments with Ceylon caoutchouc show that, under these conditions, each $C_{10}H_{16}$ unit of the molecule combines with 4 atoms of oxygen. This result is not in agreement with that obtained by Herbst (A., 1906, i, 196), and it may be assumed that the reaction which takes place when caoutchouc in benzene solution is oxidised by air (as in Herbst's experiments) differs from that which occurs when caoutchouc itself is oxidised by pure oxygen. The oxidation most probably results in the formation of additive products. W. P. S.

The Nitrogenous Constituent of Para Caoutchouc and Its Bearing on the Nature of Synthetic Caoutchouc. CLAYTON BEADLE and HENRY P. STEVENS (*J. Soc. Chem. Ind.*, 1912, 31, 1099—1101. Compare A., 1912, i, 789).—It is shown that the removal of insoluble (nitrogenous) constituents from caoutchouc results in deterioration of the latter, although it is open to question how far the quality of caoutchouc is improved by the presence of more than a certain proportion of insoluble matter. In the vulcanisation process the insoluble matter appears to play the part of a sulphur carrier.

The authors have also made experiments on the influence of the resinous constituents on the vulcanising properties of caoutchouc, and find that the removal of the resins results in a marked deterioration of the quality of the caoutchouc. The absence of nitrogenous substances and resins in synthetic caoutchouc should make the latter inferior to natural rubber.

W. P. S.

Chemistry of Caoutchouc. VI. Theory of Vulcanisation. IV. DAVID SPENCER and C. A. WARD (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 274—280. Compare A., 1912, i, 706).—Experiments have been made to ascertain whether the so-called "depolymerisation" of caoutchouc, which is brought about by mechanical or thermal treatment, is accompanied by a change in the rate at which it reacts with sulphur in the process of vulcanisation. For this purpose comparative measurements were made with two exactly similar mixtures of 100 parts of caoutchouc and 10 parts of sulphur. In the one case the caoutchouc was kneaded for thirty minutes at a moderate temperature, the sulphur being then added, and the mixing effected by a further kneading for ten minutes. In the second case, the treatment was similar, except that the caoutchouc was subjected to the mechanical treatment for ninety minutes at a much higher temperature.

From the observations made on the rate of vulcanisation at 135°, it appears that there is no appreciable difference between the two samples, and the authors draw the conclusion that "depolymerisation" has no influence whatever on the chemical result of the vulcanisation process. The conclusions arrived at by Axelrod (*Gummi Zeit.*, 1909, 24, 352) are therefore not confirmed by these experiments.

H. M. D.

The Action of Chloroacetyl Chloride on Ethyl Malonate; Iminotetronic Acid. ERICH BENARY (*Ber.*, 1912, **45**, 3682—3686). —As the substance described as the ester-amide of tetramic acid (Benary, A., 1911, i, 672) is in reality ethyl iminotetron-α-carboxylate (Anschütz, A., 1912, i, 836), the compound $C_9H_{12}O_5$, from which it is obtained by the action of ammonia, is presumably ethyl *iso*tetron-α-carboxylate; this view is supported by the action of organic bases which give compounds similar to that produced by ammonia; these compounds are probably ketonic, but do not yield phenylhydrazones (compare Wolff, A., 1900, i, 582); they frequently yield salts, however, derived from the enolic structure.

Ethyl phenyliminotetron-α-carboxylate, $\begin{matrix} CH_2\text{——}CO \\ O\cdot C(:NPh) \end{matrix}\!\!>\!CH\cdot CO_2Et$, obtained by the interaction of equivalent quantities of ethyl *iso*tetron-α-carboxylate and aniline, crystallises in needles, m. p. 116—117°; it exhibits both acidic and basic properties.

Ethyl phenylhydrazinotetron-α-carboxylate (already described) yields a *potassium* salt.

Ethyl piperidinoisotetron-α-carboxylate, $\begin{matrix} CH_2\text{——}CO \\ O\cdot C(C_5NH_{10}) \end{matrix}\!\!>\!C\cdot CO_2Et$, m. p. 107—108°, from equal weights of piperidine and ethyl *iso*tetron-

α-carboxylate, as might be expected from the structure, has no acidic properties.

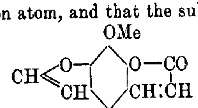
When iminotetronic acid in benzene solution is treated with rather more than an equimolecular quantity of bromine, *bromoiminotetronic acid*, $\begin{matrix} CH_2\cdot C(OH) \\ | \\ O{-}C(:NH) \end{matrix}\!\!>\!CBr$, needles, m. p. 182°, is obtained; it gives a red coloration with ferric chloride.

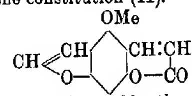
On adding ice to the reaction mixture from iminotetronic acid and nitric acid, aci-*nitroiminotetronic acid*, $\begin{matrix} CH_2{-}CO \\ | \\ O\cdot C(:NH) \end{matrix}\!\!>\!C:NO_2H$, is precipitated, leaflets, m. p. 255—258° (decomp.); it is a strongly acidic substance, which gives a *phenylhydrazone*, yellow tablets, m. p. 211—212°.

The conclusion is drawn that the action of chloroacetyl chloride on ethyl sodiomalonate consists of two concurrent processes, one of which produces unstable ethyl chloroacetylmalonate, which undergoes spontaneous change into ethyl tetron-α-carboxylate, whilst the other process involves the enolic form of ethyl sodiomalonate, which reacts with the acid chloride producing ethyl *iso*tetron-α-carboxylate. D. F. T.

Hydroxymethylfurfuraldehyde. FRANCESCO ANGELICO and A. COPPOLA (*Gazzetta*, 1912, **42**, ii, 583—589).—The authors confirm the formula for this substance given by Fenton and Gostling (T., 1889, **75**, 423), and by the application of the Angeli-Rimini reaction they have prepared from it *α-hydroxymethylfuranhydroxamic acid*, $C_6H_7O_4N$, which crystallises in pink, lustrous, soapy scales, m. p. 139°, the free acid being prepared from the *copper* salt, $(C_6H_6O_4N)_2Cu,H_2O$. When the acid is hydrolysed with 25% sulphuric acid, it yields hydroxylamine and hydroxypyromucic acid (m. p. 165°). R. V. S.

Constitution of Bergapten. HERMANN THOMS and E. BAETCKE (*Ber.*, 1912, **45**, 3705—3712).—Bergapten, which Pomeranz showed to be a coumarin-coumarone derivative of phloroglucinol (A., 1892, 71; 1893, 342), was found to occur in certain fruits accompanied by an isomeride, xanthotoxin (A., 1912, i, 40), to which the formula (I) was assigned. Bergapten has now been converted into an amine, and this into a quinone containing no methoxy-group, from which the conclusion is drawn that the methoxy-group is *para* to the unsubstituted carbon atom, and that the substance has the constitution (II).

I. 

II. 

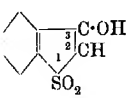
This is confirmed by the fact that xanthotoxin yields the same quinone.

Aminobergapten, $C_{12}H_7O_4\cdot NH_2$, is obtained by the reduction of the nitro-derivative (Pomeranz, *loc. cit.*) with tin and hydrochloric acid, in slender, pale yellowish-green needles, m. p. 198°, and yields an *acetyl* compound, m. p. 208°. When oxidised with sodium dichromate the

methoxy-group is replaced, and the golden-yellow *quinone*, $C_{11}H_4O_5$, m. p. 248—250°, is formed. *Aminoxanthotoxin* is prepared in the same way, and is similar in appearance to its isomeride; it melts, however, at 236°, is more easily acetylated, yielding an *acetyl* compound, m. p. 246—247°, and is much less soluble in cold sulphuric acid, but it yields the same quinone.

The *quinol*, $C_{11}H_4O_3(OH)_2$, crystallises with $2H_2O$ in light green needles, which lose water at 110°, and yield a *diacetyl* compound, m. p. 208—209°, and a *diphenylurethane* derivative, $C_{11}H_4O_3(O\cdot CO\cdot NPh_2)_2$, m. p. 229—230°. J. C. W.

Action of Hydrogen Peroxide on Hydroxythionaphthen, Hydroxythionaphthen Carboxylic Acid, and "Thioindigo." MAURICE LANFRY (*Compt. rend.*, 1912, 155, 1517—1519. Compare A., 1912, i, 293).—Hydroxythionaphthen in alkaline solution gives a blue precipitate on the addition of hydrogen peroxide, leaving a brown liquid, from which only gummy substances could be extracted. The blue precipitate on solution in water and addition of strong acid gives a red, flocculent precipitate, which resembles "thioindigo" in all its properties. The addition of hydrogen peroxide to a boiling solution of hydroxythionaphthen in acetic acid gives a red precipitate of "thioindigo," which slowly dissolves and the solution becomes colourless. Extraction with benzene separates out 3-*hydroxy*-1-*dioxythionaphthen* (annexed constitution), m. p. 139°, which in its chemical properties closely resembles the hydroxythionaphthen from which it is prepared.



The effect of hydrogen peroxide on the sodium salt of hydroxythionaphthencarboxylic acid is to destroy its phenolic character with the formation of a small quantity of "thioindigo." The major part of the salt is resinified.

In the presence of hydrogen peroxide, finely divided "thioindigo" slowly dissolves in acetic acid to a red solution, which gradually becomes decolorised. The only products of extraction were gummy substances. W. G.

"Bisphenylthiophenindigo" [5 : 5′-Diphenyl-$\Delta^{2,2'}$-bisthiophen-3-one]. PAUL FRIEDLAENDER and ST. KIELBASINSKI (*Ber.*, 1912, 45, 3389—3396).—Although *m*-hydroxydiphenyl shows no tendency to pass over into an ortho-quinonoid compound, the analogous 3-hydroxy-5-phenylthiophen behaves entirely differently, readily forming "*bisphenylthiophenindigo*," $CH{<}{CO-C{:}C\cdot CO \atop CPh\cdot S\quad S\cdot CPh}{>}CH$.

The dye is prepared by the following series of operations. On heating ethyl cinnamate with sulphur, a disulphide, thiobenzoylthioacetic acid, $S{<}{S-CO \atop CPh{:}CH}$ (Baumann and Fromm, A., 1897, i, 191), is formed. The ring is opened by sodium sulphide, and by the action of chloroacetic acid a compound,

$$CO_2H\cdot CH_2\cdot S\cdot CPh{:}CH\cdot CO\cdot S\cdot CH_2\cdot CO_2H,$$

is formed, which when boiled with acetic anhydride is converted into acetoxyphenylthiophen, $S<\begin{matrix}CH-C\cdot O\cdot CO\cdot CH_3\\ CPh:CH\end{matrix}$. On hydrolysis, 4-hydroxy-2-phenylthiophen is obtained.

This condenses with aromatic aldehydes or with isatin to dyes, forms a quinoneoxime with nitrous acid, and is converted by alkaline or acid oxidising agents into "bisphenylthiophenindigo."

The *disulphide* crystallises in broad needles, m. p. 156°.

4-*Hydroxy-2-phenylthiophen* separates in slender needles, m. p. 78°; the *acetyl* derivative forms broad, colourless, compact platelets, m. p. 75°.

The *quinone oxime*, $S<\begin{matrix}CPh=\!=\!=CH\\ C(:N\cdot OH)\cdot CO\end{matrix}$, prepared by interaction with sodium nitrite, forms broad faint, brownish-yellow needles, m. p. 216°.

On bromination, a *product*, $CPh<\begin{matrix}CBr\cdot CO\\ S-\!-CBr_2\end{matrix}$, is obtained, crystallising in brownish-yellow plates, m. p. 134°. It does not react simply with aniline: on warming with sodium acetate, slender, red needles or ruby-red prisms of a brominated diphenylthiophenindigo are obtained.

4-Hydroxy-2-phenylthiophen reacts with piperonal, the *condensation* product crystallising in long, yellow needles, m. p. 196°.

"*Bis-5-phenyl-2-thiophenindigo*" [5 : 5'-*diphenyl*-$\Delta^{2,2'}$-*bisthiophen*-3-*one*] separates in brownish-red, lustrous needles, m. p. 280°.

"5-*Phenyl-2-thiophen-3-indoleindigo*" [5-phenyl-2-(3'-indoxyl)-thiophen-3-one], produced on condensation with isatin, crystallises in sealing wax-red needles, m. p. 281°.

"5-*Phenyl-2-thiophen-2-indoleindigo*" [5-phenyl-2-(2'-indoxyl)-thiophen-3-one], $\begin{matrix}CH\cdot CO\\ \parallel\\ CPh\cdot S\end{matrix}>C:C<\begin{matrix}CO\\ NH\end{matrix}>C_6H_4$, obtained on boiling isatin-anilide with phenylhydroxythiophen in acetic anhydride, crystallises in slender, dark violet needles. E. F. A.

Methylation of Histidine, Arginine, and Lysine. I. R. ENGELAND and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1912, 59, 415—419).—On methylation of histidine monochloride with methyl sulphate and barium hydroxide, *pentamethylhistidine* is obtained. The *aurichloride* crystallises in large, lustrous needles, the *chloride* is an oil, and the free base decomposes rapidly. Small quantities of the crystalline *aurichloride* of tetramethylhistidine are obtained at the same time.

Under similar conditions, arginine yields a *tetramethyl* derivative, the *aurichloride* forms short, stout needles, m. p. 173—175°. Three of the methyl groups are attached to nitrogen in the side-chain, one only to nitrogen in the guanidine complex.

Lysine yields a compound, probably the *ethyl* ester of *hexamethyllysine*, which gives an *aurichloride*, m. p. 208°, corresponding with the formula $C_{14}H_{34}O_3N_2,Au_2Cl_8$. E. F. A.

Strychnos Alkaloids. XVI. Dihydrobrucinoic Acid and *iso*Brucinolone. HERMANN LEUCHS and GEORGE PEIRCE (*Ber.*, 1912, 45, 3412—3420).—Dihydrobrucinonic acid, which contains an alcoholic

hydroxyl (compare A., 1212, i, 210), forms an acetyl derivative when acted on by acetic anhydride and sodium acetate. More vigorous action produces a neutral compound containing two further acetyl residues less a molecule of water. Dihydrobrucinonic acid does not react with nascent hydrogen or with hydroxylamine. It is broken down by sodium hydroxide into glycollic acid and *iso*brucinolone, $C_{21}H_{22}O_5N_2$. The latter forms an acetyl derivative, and on treatment with concentrated hydrogen chloride gives iso*brucinolone hydrate*. At higher temperatures this is reconverted into *iso*brucinolone (compare Leuchs and Brewster, A., 1912, i, 210). With concentrated nitric acid a nitro-derivative, $C_{19}H_{15}O_7N_3$, is obtained; the change involves the formation of a quinone and the subsequent nitration of this. With sulphurous acid a paler reduction compound is obtained from the quinone.

Acetyldihydrobrucinonic acid forms colourless, four-sided prisms, m. p. 235—238°. The neutral product, $C_{27}H_{28}O_9N_2$ or $C_{29}H_{30}O_{10}N_2$, crystallises in colourless, chisel-shaped prisms, m. p. 280—282°, after becoming yellow at 260°.

By the action of acetic anhydride on brucinonic acid, a componnd,

$$(C_{13}H_{14}O_4N)_x,$$

is obtained, crystallising in long, matted, lustrous needles, m. p. 125—127°.

*Acetyl*iso*brucinolone* forms large, colourless platelets, m. p. 281—283° (decomp.).

iso*Brucinolone hydrate* separates in four-sided prisms, which froth at 205—208°, become solid again, turn brown at 290°, m. p. 310—315° (decomp.).

The *hydrochloride* forms four-sided platelets; the *sulphate* consists of massive prisms, which become brown at 235°, decomp. 238°.

*Nitrobis*apo*methyldihydro*iso*brucinolone* crystallises in flat, orange-yellow needles, which become brown at 250°, and completely charred at 340°.

*Nitrobis*apo*methyl*iso*brucinolone* gives massive, reddish-yellow prisms, which become brown at 240°.

*Nitrobis*apo*methylbrucinolone* crystallises in small, yellow octahedra, dissolving in concentrated sulphuric acid with a yellow coloration and in concentrated sodium hydroxide with a violet coloration.

E. F. A.

Strychnos Alkaloids. XVII. Isolation of the Hydrate of a Fourth Strychninesulphonic Acid. HERMANN LEUCHS and JOHANNES WUTKE (*Ber.*, 1912, **45**, 3686—3691).—Analogous to the fourth brucinesulphonic acid (Leuchs and Geiger, A., 1911, i, 1018), a fourth strychninesulphonic acid (compare Leuchs and Schneider, A., 1909, i, 671) has been obtained as a very stable hydrate, which retains the additional water very tenaciously.

The solution of the reaction product obtained as described earlier (Leuchs and Schneider, *loc. cit.*), after crystallisation of strychnine-sulphonic acids I and II, and subsequent concentration under reduced pressure, deposits a mixture of the acids I, II, and III with the above-mentioned hydrate, which last can be separated in the free

state and also as a compound with strychninesulphonic acid III; the total yield of hydrate in the two forms amounts to approximately 3%.

Strychninesulphonic acid IV *hydrate*, $C_{21}H_{24}O_6N_2S,2H_2O$, stout prisms or rhombohedra, m. p. 275° (decomp.), $[\alpha]_D^{20}$ +18·3°, could not be dehydrated beyond $C_{21}H_{24}O_6N_2S$, even at 135° in a vacuum over phosphoric oxide. The *double* compound with strychninesulphonic acid III, $C_{21}H_{22}O_5N_2S,C_{21}H_{24}O_6N_2S$, slender prisms or needles, m. p. 250° (decomp.), $[\alpha]_D^{20}$ +101°, can also be obtained by mixing solutions of the hydrate and excess of the acid III; in the absence of excess of strychninesulphonic acid III, the compound is resolved by hot water into its constituents. D. F. T.

Synthesis of Hæmopyrrole-*b*. OSKAR PILOTY and A. BLÖMER (*Ber.*, 1912, **45**, 3749—3753).—Ethyl acetylpyruvate condenses with aminobutanone or with aminoacetone to form pyrrole derivatives. In the former case, 4-acetyl-2 : 3-dimethylpyrrole-5-carboxylic acid,

$$NH<\begin{matrix}C(CO_2H):C\cdot COMe\\ CMe{=\!=}CMe\end{matrix},$$

is obtained, which on heating at 215° is converted into 4-*acetyl*-2 : 3-*dimethylpyrrole*, $NH<\begin{matrix}CH{=}C\cdot COMe\\ CMe:CMe\end{matrix}$. When this is treated with hydrazine and sodium ethoxide, 2 : 3-dimethyl-4-ethylpyrrole (hæmopyrrole-*b*), $NH<\begin{matrix}CH{=}CEt\\ CMe:CMe\end{matrix}$, is formed.

With aminoacetone the product is 4-*acetyl*-3-*methylpyrrole*-5-*carboxylic acid*, $NH<\begin{matrix}C(CO_2H):C\cdot COMe\\ CH{=\!=}CMe\end{matrix}$. This has m. p. 200°. During the reaction an isomeric by-product, m. p. 250° (decomp.), is also formed.

4-*Acetyl*-2 : 3-*dimethylpyrrole*-5-*carboxylic acid* crystallises in colourless, prismatic rods, m. p. 204° (decomp.).

4-*Acetyl*-2 : 3-*dimethylpyrrole* separates in short, colourless, prismatic platelets with sharp edges, m. p. 137°. The synthetic hæmopyrrole-*b* is identical with the natural compound. E. F. A.

Cyclic Imines. VII. Ahrens' So-called γ-Picoline. JULIUS VON BRAUN and A. SCHMATLOCH (*Ber.*, 1912, **45**, 3649—3652).—The method described by Ahrens for the separation of pure 4-methylpyridine (γ-picoline) by precipitation with mercuric chloride (A., 1905, i, 232) is found to yield a mixture instead of a pure product.

Successive reduction and benzoylation of 4-methylpyridine, prepared by Ahrens' method, produced a *benzoyl* derivative, $C_6H_{12}NBz$, b. p. 189—190°/17 mm., which on distillation with phosphorus pentabromide (compare von Braun and Sobecki, A., 1911, i, 413) formed a product which could be separated into two fractions by distillation. The smaller and less volatile portion, b. p. 150°/19 mm., D_4^{20} 1·9305, was probably *αβε-tribromo-β-methylpentane*, and gave an unsaturated organo-magnesium compound which absorbed carbon dioxide with the formation of *δ-methylene*-n-*hexoic acid*, $CO_2H\cdot[CH_2]_3\cdot CMe:CH_2$, b. p. 218—221°, D_4^{20} 0·9406, n_D 1·4442; the formation of this series of compounds is attributed to the presence of 3-methylpyridine in the

original base. The more volatile fraction, $C_6H_{12}Br_2$, b. p. 115—120°/19 mm., D_4^{20} 1·608, on treatment with potassium cyanide yielded a dinitrile, $C_6H_{12}(CN)_2$, b. p. 171—174°/10 mm., which was hydrolysable, apparently to a mixture of β- and γ-methylpimelic acids. Neither fraction therefore was of pure 4-methylpyridine. D. F. T.

The Action of Hydroxylamine and Phenylhydrazine on Benzoyldehydracetic Acid. A Correction. JOH. SCHÖTTLE (*Ber.*, 1912, **45**, 3779. Compare A., 1912, i, 915).—Reaction between free hydroxylamine and benzoyldehydracetic acid was effected by mixing hydroxylamine sulphate with the theoretical quantity of alcoholic potassium hydroxide, filtering the precipitated potassium sulphate, and adding the phenyl-lactam of benzoyldehydracetic acid to the filtrate.

E. F. A.

Cyclic Imines. VI. Ring Homologues of Tetrahydroquinoline. JULIUS VON BRAUN and B. BARTSCH (*Ber.*, 1912, **45**, 3376—3389).—The tendency to form seven-membered rings such as hexamethyleneimine is very much increased when two of the carbon atoms are members of a benzene nucleus; thus *o*-δ-chlorobutylaniline, on elimination of hydrogen chloride, readily forms *tetrahydrohomoquinoline*, $C_6H_4<\begin{smallmatrix}CH_2\cdot CH_2\\NH-CH_2\end{smallmatrix}>CH_2$. The constitution of the quinoline is established by the fact that when the ring is opened by the action of phosphorus pentachloride, δ-chloro-*o*-benzoylaminobutylbenzene, $COPh\cdot NH\cdot C_6H_4\cdot[CH_2]_4Cl$, is formed, which is in turn convertible into the already known δ-*o*-benzoylaminophenylvaleric acid.

Homotetrahydroquinoline resembles the isomeric 2-methyltetrahydroquinoline and the lower ring homologues in its stability towards hydrolytic and reducing reagents, and also towards oxidation; it is hardly altered by distillation with silver sulphate.

The quinoline could not be prepared by other methods, such as the distillation of δ-*o*-diaminobutylbenzene hydrochloride or by the interaction of γ-phenylpropylamine with formaldehyde.

o-*Amino-δ-hydroxybutylbenzene*, $NH_2\cdot C_6H_4\cdot[CH_2]_4\cdot OH$, prepared by the reduction of the ester, $NH_2\cdot C_6H_4\cdot[CH_2]\cdot CO_2Et$, by means of sodium and alcohol, is a viscid, almost odourless oil, b. p. 180—183°/12 mm. The *dibenzoyl* compound crystallises in snow-white platelets which sinter at 127°, m. p. 130°; the *platinichloride* forms dark red platelets, which blacken at 168°, m. p. 175°; the *picrate* separates in green leaflets, m. p. 179°.

o-*Amino-δ-chlorobutylbenzene* was not obtained pure; the *platinichloride* crystallises in pale yellow platelets, m. p. 182—183°.

Tetrahydrohomoquinoline is an almost colourless oil, b. p. 131—133°/16 mm., 253—255°/760 mm., D_4^{20} 1·0325, solidifying to colourless crystals, m. p. 32°. The *hydrochloride* has m. p. 186°; the pale yellow, granular crystals of the *platinichloride* blacken at 192°, m. p. 194°; the *picrate* crystallises in yellowish-red needles, m. p. 179°; the *benzoyl* derivative has m. p. 96°, whilst the *benzenesulphonyl* compound has m. p. 109°.

The *platinichloride* of the *dimethyl* derivative, $C_{10}H_{12}NMe_2PtCl_6$, produced on long heating with methyl iodide, has m. p. 197°.

When heated with phosphorus pentachloride at 150°, tetrahydrohomoquinoline yields *δ-chloro-o-benzoylaminobutylbenzene*, which crystallises in lustrous, silvery platelets, m. p. 117°. The corresponding iodide when decomposed with potassium cyanide yields *δ-benzoylaminophenylvaleronitrile*, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot [CH_2]_4 \cdot CN$, m. p. 114°, from which the corresponding acid (A., 1907, i, 524) is obtained on hydrolysis.

δ-o-*Diaminobutylbenzene*, prepared by reducing the nitrile of *o*-benzoylaminophenylbutyric acid, forms a colourless oil of strongly basic odour, b. p. 172°/14 mm.

o-γ-*Chloropropylbenzonitrile* is a pale yellow oil, volatile in steam, b. p. 153°/19 mm. On hydrolysis, o-γ-*chloropropylbenzoic acid*,

$$CO_2H \cdot C_6H_4 \cdot [CH_2]_3 \cdot Cl,$$

is obtained, m. p. 79°.

The nitrile condenses with sodium phenoxide to o-γ-*phenoxypropylbenzonitrile*, $CN \cdot C_6H_4 \cdot [CH_2]_3 \cdot OPh$, a pale yellow oil, b. p. 210°/23 mm. The corresponding o-γ-*phenoxypropylbenzoic acid* has m. p. 120°. E. F. A.

Thiazoles. Reinhold von Walther and H. Roch (*J. pr. Chem.*, 1913, [ii], 87, 27—66).—Although the condensation of thiocarbamide with ω-bromoacetophenone and other halogeno-ketones of the type CHXR·COR may give rise to either aminothiazoles (formula II below, R′ and R″ = H) or iminothiazolines (IV or V, R′,R″ = H), the work of Traumann (A., 1889, 414) and others has shown that only aminothiazoles are produced. *s*-Disubstituted thiocarbamides always yield iminothiazolines, whilst the *as*-disubstituted derivatives give rise to aminothiazoles.

With respect to the mechanism of the condensation, the authors suggest that the first stage consists in the addition of the halogeno-ketone to the sulphur atom of the thiocarbamide, and that the removal of hydrogen haloid and water from the intermediate compound thus produced is preceded by the formation of an internal salt, derived from the enolic form, the constitution of this salt being determined by the relative basicity of the amino-residues of the thiocarbamide; thus, in the condensation of *as*-disubstituted thiocarbamides,

$$NR'R'' \cdot CS \cdot NH_2,$$

with ω-bromoacetophenone, the compound

$$NR'R'' \cdot C(NH_2) \colon SBr \cdot CH_2 \cdot COPh$$

is first produced, which is transformed successively into the enolic salt I and aminothiazole II if NHR′R″ is more feebly basic than NH_3:

$$\text{I.}\ \begin{array}{l} NR'R'' \cdot C{-}NH_3{-}O \\ \qquad\quad \| \qquad\quad | \\ \qquad\quad SBr \cdot CH \colon CPh \end{array} \longrightarrow \text{II.}\ \begin{array}{l} NR'R'' \cdot C{=\!=}N \\ \qquad\quad | \qquad\ | \\ \qquad\quad S \cdot CH \colon CPh \end{array} + H_2O + HBr.$$

On the other hand, if NHR′R″ is a stronger base than NH_3, the compound III is formed as an intermediate product, which decomposes

into a secondary amine and thiocyanoacetophenone as shown in the following scheme:

$$\text{III.}\ \begin{array}{l}\text{NHR}'\text{R}''\text{—C·NH}_2\\ \text{O·CPh:CH·SBr}\end{array} \longrightarrow \text{HBr} + \text{H}_2\text{O} +$$
$$\begin{array}{l}\text{NR}'\text{R}''\text{—CN}\\ \text{CPh:CH·S}\end{array} \xrightarrow{\text{H}_2\text{O}} \text{NHR}'\text{R}'' + \text{OH·CPh:CH·SCN}.$$

An explanation is thus afforded of the behaviour of *as*-dimethylthiocarbamide, which, with ω-bromoacetophenone, does not form an aminothiazole, but undergoes decomposition into dimethylamine and thiocyanoacetophenone (Spica and Carrara, A., 1892, 215).

s-Disubstituted thiocarbamides, $\text{NHR}'\text{·CO·NHR}''$, in which the amino-residues are of approximately equal basicity, may give rise to two isomeric iminothiazolines:

$$\text{IV.}\ \begin{array}{l}\text{CPh·NR}''\\ \text{CH——S}\end{array}\!\!>\text{C:NR}' \qquad \text{V.}\ \begin{array}{l}\text{CPh·NR}'\\ \text{CH——S}\end{array}\!\!>\text{C:NR}'';$$

the formation of isomerides of this kind has been observed by Stenz (*Diss.*, Dresden, 1899) and Wünsche (*ibid.*, 1901). When the basicity of one of the amino-groups is much greater than that of the other, only one isomeride will be formed; thus, both *s*-*p*-tolylbenzylthiocarbamide and *s*-*p*-tolylmethylthiocarbamide condense with ω-bromoacetophenone to form only one iminothiazoline (formula V, where $\text{R}'' = p\text{-C}_6\text{H}_4\text{Me}$, and $\text{R}' = \text{·CH}_2\text{Ph}$ or Me). The constitution of the iminothiazolines derived from *s*-disubstituted thiocarbamides is readily determined (1) by heating with carbon disulphide, which leads to the removal of the imino-group as the corresponding thiocarbimide, or (2) by hydrolysis with hydrochloric acid, the imino-group, in this case, being removed in the form of a primary amine.

With respect to the thiazoles derived from mono-substituted thiocarbamides, the authors point out that no definite proof of their constitution has hitherto been brought forward. Although the work of Traumann (*loc. cit.*) appears to indicate that the thiazole obtained from methylthiocarbamide and ω-bromoacetophenone is probably a 2-methylimino-4-phenylthiazoline, the observations described in the present paper prove conclusively that the thiazole derived from *p*-tolylthiocarbamide has the constitution of an aminothiazole.

2-p-*Toluidino-4-phenylthiazole*, $\begin{array}{l}\text{CPh·N}\\ \text{CH—S}\end{array}\!\!>\text{C·NH·C}_6\text{H}_4\text{Me}$, is obtained in the form of its *hydrobromide*, slender needles, m. p. 205° (decomp.), by heating *p*-tolylthiocarbamide with ω-bromoacetophenone in alcoholic solution, the free base being liberated from the hydrobromide by warming with pyridine. It crystallises in leaflets, m. p. 123°, and forms a *hydrochloride*, which melts and becomes green at 212°, a *sulphate*, m. p. 152°, an *acetate*, m. p. 85°, and *thiocyanate*, m. p. 125°, all of which crystallise in colourless needles; the *platinichloride* forms orange leaflets, m. p. 230°, the *picrate*, yellow needles, m. p. 185°. It reacts with phenylcarbimide in ethereal solution to form the *carbamide*, $\begin{array}{l}\text{CPh·N}\\ \text{CH—S}\end{array}\!\!>\text{C·N(C}_6\text{H}_4\text{Me)·CO·NHPh}$, crystallising in lustrous leaflets,

m. p. 196·5°. Towards both oxidising and reducing agents the thiazole is remarkably stable, but is decomposed by hydrochloric acid at 225—250° into acetophenone, *p*-toluidine, and ammonia; when heated with carbon disulphide at 250°, it forms *p*-tolylthiocarbimide.

The *acetyl* derivative, $C_{18}H_{16}ON_2S$, forms colourless prisms, m. p. 124·5°; the *benzoyl* derivative, prepared by the pyridine method in benzene solution, crystallises in hard prisms, m. p. 207°.

With the object of synthesising the above acyl derivatives, the authors have endeavoured to condense ω-bromoacetophenone with *s*- and *as*-acetyl-*p*-tolylthiocarbamide and *s*-benzoyl-*p*-tolylthiocarbamide in alcoholic solution, but find that no condensation occurs. It would thus appear that acylthiocarbamides are incapable of undergoing the thiazole condensation.

2-*p*-Toluidino-4-phenylthiazole combines with 1-chloro-2 : 4 : 6-trinitrobenzene in hot alcoholic solution to form an unstable, additive *compound*, $C_{22}H_{16}O_6N_5SCl$, which crystallises in red needles, m. p. about 90°, and is resolved by acids or alkalis into its components; the additive *compound* with 1-chloro-2 : 4-dinitrobenzene forms stout, dark red crystals, m. p. about 60°.

as-p-*Tolylbenzylthiocarbamide*, $C_6H_4Me\cdot N(CH_2Ph)\cdot CS\cdot NH_2$, obtained by heating *N*-benzyl-*p*-toluidine hydrochloride with ammonium thiocyanate and water, crystallises in colourless needles, m. p. 155·5°, and is converted by the action of ω-bromoacetophenone in warm alcoholic solution into 2-p-*tolylbenzylamino-4-phenylthiazole*,

$$\begin{matrix}CPh\cdot N\\ \| \\ CH-S\end{matrix}\!\!>C\cdot N(C_6H_4Me)\cdot CH_2Ph,$$

which forms large prisms, m. p. 125°, and yields a *hydrochloride*, a *picrate*, m. p. 155°, and a *platinichloride*, m. p. 225° (decomp.).

2-p-*Tolylimino-4-phenyl-3-benzylthiazoline*,

$$\begin{matrix}C_6H_4Me\cdot N:C & \!\!-\!\!-\!\!-\!\!-\!\! & N\cdot CH_2Ph\\ | & & | \\ S\cdot CH & : & CPh\end{matrix},$$

prepared from *s*-*p*-tolylbenzylthiocarbamide and ω-bromoacetophenone, forms colourless needles, m. p. 152°; the *hydrochloride*, *platinichloride*, m. p. 233° (decomp.), and *picrate*, m. p. 155°, are described. That the compound has the above constitution, and not that of the isomeric 2-benzylimino-4-phenyl-3-*p*-tolylthiazoline, has been established by its behaviour towards carbon disulphide, which at 200° leads to the removal of the *p*-tolylimino-group as *p*-tolylthiocarbimide and the formation of 2-*thion-4-phenyl-3-benzylthiazoline*, $\begin{matrix}S-\!\!-CS\\ | \\ CH:CPh\end{matrix}\!\!>N\cdot CH_2Ph$, which crystallises in pale yellow needles, m. p. 101°.

When heated with benzyl chloride for eight hours at 175°, 2-*p*-toluidino-4-phenylthiazole yields 2-p-*tolylbenzylamino-4-phenyl-5-benzylthiazole*, $\begin{matrix}CPh-\!\!-\!\!-N\\ \| \\ C(CH_2Ph)\cdot S\end{matrix}\!\!>C\cdot N(C_6H_4Me)\cdot CH_2Ph$. This forms needles, m. p. 125°, and is accompanied by 2-p-*toluidino-4-phenyl-5-benzylthiazole*, $\begin{matrix}CPh-\!\!-\!\!-N\\ \| \\ C(CH_2Ph)\cdot S\end{matrix}\!\!>C\cdot NH\cdot C_6H_4Me$, which crystallises in needles, m. p. 174°, and yields a *platinichloride*, m. p. 203° (decomp.), and a *picrate*, m. p. 151°.

That the introduction of the benzyl group has taken place in the thiazole ring and not in the *p*-toluidino-residue has been proved in the case of the last-mentioned thiazole by the formation of an *acetyl* derivative, $C_{25}H_{22}ON_2S$, m. p. 144°, and also by the removal of the *p*-tolylimino-group as *p*-tolylthiocarbimide when the thiazole is heated with carbon disulphide.

2-p-*Tolylimino-4-phenyl-3-methylthiazoline*,

$$\begin{array}{l}CPh\cdot NMe\\ \|\\ CH\text{——}S\end{array}\!\!>C{:}N\cdot C_6H_4Me,$$

obtained in the form of its *methiodide*, large needles, m. p. about 200° (decomp.), by heating 2-*p*-toluidino-4-phenylthiazole with methyl iodide in methyl alcoholic solution, crystallises in colourless leaflets, m. p. 118°. It has also been prepared by the condensation of *s*-*p*-tolylmethylthiocarbamide with ω-bromoacetophenone; the *hydrochloride* and *picrate*, m. p. 158°, are described. When heated with carbon disulphide, it yields *p*-tolylthiocarbimide and 2-*thion-4-phenyl-3-methylthiazoline*, $\begin{array}{l}CS\cdot NMe\\ |\\ S\text{——}CH\end{array}\!\!>CPh$, which crystallises in pale yellow needles, m. p. 127°.

2-p-*Tolylimino-4-phenyl-5-benzyl-3-methylthiazoline*,

$$\begin{array}{l}CPh\text{—}NMe\\ \|\\ C(CH_2Ph)\cdot S\end{array}\!\!>C{:}N\cdot C_6H_4Me,$$

prepared by the action of methyl iodide on 2-*p*-tolylimino-4-phenyl-5-benzylthiazole, forms colourless prisms, m. p. 151°, and yields a *hydrochloride*, and a *methiodide*, crystallising in needles, m. p. about 250° (decomp.). It is resolved by carbon disulphide into *p*-tolylthiocarbimide, and 2-*thion-4-phenyl-5-benzyl-3-methylthiazoline*, $\begin{array}{l}NMe\cdot CPh\\ |\\ CS\text{——}S\end{array}\!\!>C\cdot CH_2Ph$, which forms silvery, lustrous leaflets, m. p. 116°.

5-*Bromo-2-p-toluidino-4-phenylthiazole*, obtained by brominating 2-*p*-toluidino-4-phenylthiazole in benzene solution, crystallises in colourless leaflets or needles, which melt and decompose at 134°, yielding *p*-tolylthiocarbimide; the *hydrobromide*, m. p. 179° (decomp.), and *acetyl* derivative, m. p. 142·5°, crystallise in colourless prisms. It is reduced by zinc and acetic acid to the original thiazole. Attempts to prepare the bromothiazole by the condensation of *p*-tolylthiocarbamide with di-ω-bromoacetophenone yielded a *substance*, m. p. 142° (decomp.).

When warmed with amyl nitrite in alcoholic solution, 2-*p*-toluidino-4-phenylthiazole yields the 5-*nitroso*-derivative,

$$\begin{array}{l}CPh\text{—}N\\ \|\\ C(NO)\cdot S\end{array}\!\!>S\cdot NH\cdot C_6H_4Me.$$

This separates in yellowish-brown leaflets, m. p. 184° (decomp.), yields a *hydrochloride*, red needles, an *acetyl* derivative, lustrous, dark red leaflets, m. p. 163°, and is reduced by zinc and acetic acid in alcoholic solution to the corresponding *amino*-compound, which, however, could not be isolated in a pure condition.

On treatment with cold aqueous alkalis it becomes brown, probably owing to the formation of salts derived from the tautomeric form (see VI, next page); when boiled with aqueous alkalis it undergoes com-

plete decomposition, yielding hydrogen sulphide, *p*-tolylthiocarbimide, carbon dioxide, thiocyanic acid, benzoic acid, ammonia, and *p*-toluidine.

The *silver* salt, $C_{16}H_{12}ON_3SAg$, prepared by treating an alcoholic solution of the nitroso-compound with the equivalent amounts of ammonia and silver nitrate, separates as an indistinctly crystalline, red precipitate which readily decomposes and explodes when rapidly heated.

On treatment with benzoyl chloride, a solution of the nitroso-compound in aqueous alkalis yields benzoyl-*p*-tolylcyanamide (Heller and Bauer, A., 1902, i, 444), benzoic and thiocyanic acids. This reaction, which establishes the position of the nitroso-group in the thiazole ring, takes place according to the following scheme:

$$\text{VI.}\quad C_6H_4Me{\cdot}N{:}\overset{\text{N:CPh}}{\underset{|}{C}}{-}{-}S{>}C{:}NOH \xrightarrow{H_2O+BzCl}$$

$$C_6H_4Me{\cdot}NBz{\cdot}C({:}NH){\cdot}S{\cdot}C({:}NOH){\cdot}COPh \longrightarrow$$

$$C_6H_4Me{\cdot}NBz{\cdot}C{:}N + HS{\cdot}C{:}N + OH{\cdot}COPh.$$

5-*Bromo*-2-p-*tolylnitrosoamino*-4-*phenylthiazole*,

$$\begin{matrix} CPh{\cdot}N \\ \| \\ CBr{-}S \end{matrix}{>}C{\cdot}N(C_7H_7){\cdot}NO,$$

prepared by warming 5-bromo-2-*p*-toluidino-4-phenylthiazole with amyl nitrite, forms colourless needles, m. p. 220°.

2-*p*-Toluidino-4-phenylthiazole combines with benzenediazonium chloride in alcoholic solution, yielding 5-*benzeneazo*-2-p-*toluidino*-4-*phenylthiazole*, $C_6H_4Me{\cdot}NH{\cdot}\begin{matrix} N{\cdot}CPh \\ \| \\ C{-}{-}{-}S \end{matrix}{>}C{\cdot}N{:}NPh$, which crystallises in orange-red needles, m. p. 191°, and forms an *acetyl* derivative, $C_{24}H_{20}ON_4S$, red prisms, m. p. 217°, and a *hydrochloride*, crystallising in dark violet-red needles having a greenish glance, m. p. 184° (decomp.).

5-p-*Nitrobenzeneazo*-2-p-*toluidino*-4-*phenylthiazole*, obtained in a similar manner from *p*-nitrobenzenediazonium chloride, crystallises in dark red needles, m. p. 245° (decomp.); the *hydrochloride*, reddish-violet needles, and *acetyl* derivatives, red needles, both melt indefinitely at 250°.

The authors have also studied the behaviour of the remaining aminothiazoles and iminothiazolines described in this paper towards diazonium salts, and find that the iminothiazolines in no circumstances couple with the diazonium salts, whilst the aminothiazoles, in which the 5-position is unsubstituted, readily combine, yielding azo-compounds. The behaviour of 5-bromo-2-*p*-toluidino-4-phenylthiazole is, however, exceptional, the action of benzenediazonium chloride leading to the removal of the bromine atom and the formation of the above-mentioned 5-benzeneazo-2-*p*-toluidino-4-phenylthiazole. The reaction towards diazonium salts thus furnishes a ready means of distinguishing whether the product obtained by the condensation of a monosubstituted thiocarbamide with ω-bromoacetophenone and analogous halogeno-ketones is an aminothiazole or iminothiazoline.

2-p-*Toluidino*-4 : 5-*diphenylthiazole*, $\begin{matrix} CPh{\cdot}N \\ \| \\ CPh{\cdot}S \end{matrix}{>}C{\cdot}NH{\cdot}C_6H_4Me$, pre-

pared from desyl bromide and *p*-tolylthiocarbamide, crystallises in colourless needles, m. p. 178°, and forms a *hydrochloride*.

The condensation of ω-bromoacetophenone and allylthiocarbamide yields *2-allylamino-4-phenylthiazole*, $\begin{matrix} CPh\cdot N \\ \| \quad\quad \\ CH-S \end{matrix}\!\!>C\cdot NH\cdot C_3H_5$, which has m. p. 73°, and couples with diazonium salts to form red azo-compounds. F. B.

Decomposition of Alkylidenehydrazines. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1754—1759).—*Menthylidenehydrazine*, $CH_2<\begin{matrix} CH_2\cdot CHPr \\ CHMe\cdot CH_2 \end{matrix}>C:N\cdot NH_2$, is a colourless liquid, b. p. 144°/30 mm., 248—249°/759 mm., D_0^{20} 0·9333, n_D 1·4940, $[\alpha]_D - 52{\cdot}45°$. When distilled under reduced pressure, it leaves a viscous residue which, on treatment with 10% sulphuric acid in the cold, yields menthone and *l*-menthazine (compare A., 1908, i, 91). Pure menthylidenehydrazine yields no menthazine with cold 10% sulphuric acid, the sole product being menthone, which exhibits a low specific rotation owing to partial inversion. Distillation of the base with platinised porous tile yields hydrazine and *l*-menthazine. Menthylidenehydrazine is slightly decomposed, with evolution of nitrogen, when distilled with fused potassium hydroxide, whilst in presence of both platinised porous tile and fused alkali, it is resolved into nitrogen and menthane.

iso*Thujylidenehydrazine*, $CMe<\begin{matrix} CHPr^\beta\cdot CH_2 \\ CMe-C:N\cdot NH_2 \end{matrix}$, prepared from *iso*thujane and hydrazine hydrate, is a faint yellow, viscous liquid, b. p. 143—144°/17 mm., 152—153°/25 mm., D_0^{20} 0·9579, n_D 1·5328. Distillation of the base in presence of potassium hydroxide, spongy platinum, or molecular silver yields (1) nitrogen, (2) hydrazine, (3) a mixture of the hydrocarbons, $C_{10}H_{18}$ and $C_{10}H_{16}$, giving a cherry-red coloration with sulphuric acid and acetic anhydride and a green one with sulphuric acid and methyl alcohol, and (4) iso*thujazine*,

$$C_{10}H_{16}:N_2:C_{10}H_{16},$$

which crystallises in golden-yellow needles, m. p. 161—162°.

When distilled with potassium hydroxide, carvylidenehydrazine yields a *hydrocarbon*, $C_{10}H_{16}$, b. p. 175—176°/749 mm. (175—176°/757 mm.), D_0^{20} 0·8361 (0·8349), n_D 1·4678 (1·4665), $[\alpha]_D - 36{\cdot}74°$ ($-35{\cdot}36°$), which with hydrogen bromide gives the *dipentene hydrobromide*, $C_{10}H_{16},2HBr$, m. p. 63°, and with ethyl nitrite and hydrochloric acid, *l*-limonene β-nitrosochloride. T. H. P.

Hydantoins. XX. Action of Thiocyanates on α-Amino-acids. TREAT B. JOHNSON (*Amer. Chem. J.*, 1913, 49, 68—69).—It has been shown in earlier papers that by the action of thiocyanates on acyl derivatives of α-amino-acids, acylthiohydantoins are produced. The author has now found that the salt used in certain experiments (A., 1912, i, 53, 316, 390, 807) which was supposed to be potassium thiocyanate was really the ammonium salt, and the yields recorded were therefore obtained from the latter. The two salts show a remarkable difference in their behaviour with hippuric acid; the same com-

pound is formed in each case, but with the potassium salt it is obtained as an oily product which only slowly solidifies, whilst when prepared from the ammonium salt it solidifies at once on being poured into water. E. G.

Tetraphenyldi-iminotetrahydromiazthiole (3:5-Diphenylimino-1:4-diphenyltetrahydro-1:2:4-thiodiazole). EMIL FROMM [with WILHELM BITTERICH] (*Annalen*, 1912, 394, 284—290).—3:5-Diphenylimino-1:4-diphenyltetrahydro-1:2:4-thiodiazole is probably a direct product of the oxidation of diphenylthiocarbamide, and is not formed through the intermediate production of an unstable disulphide (compare Fromm and Heyder, A., 1909, i, 903). It is best prepared by Hugershoff's method of oxidation by alcoholic bromine, care being taken to work in the cold, otherwise triphenylguanidine is obtained. The substance is converted into triphenylguanidine by concentrated hydrochloric acid, and is decomposed by boiling glacial acetic acid into acetanilide and 1-anilinobenzothiazole. By heating with aniline at 110° for several hours, the diphenyliminodiphenyltetrahydrothiodiazole is converted into the isomeric *triphenylguanidobenzothiazole*, $NHPh\cdot C(:NPh)\cdot NPh\cdot C{<}{}^{N}_{S}{>}C_6H_4$, m. p. 142°, which is not desulphurised by lead oxide and an alkali, and yields by the Schotten-Baumann process *2-benzoylphenylaminobenzothiazole*,

$$C_6H_4{<}{}^{N}_{S}{>}C\cdot NPh\cdot COPh,$$

m. p. 156°, which is also obtained from 2-anilinobenzothiazole, benzoyl chloride, and aqueous sodium hydroxide. C. S.

Trimethylparamide. HANS MEYER and KARL STEINER (*Ber.*, 1912, 45, 3676—3677. Compare Mumm and Bergell, A., 1912, i, 1015).—Trimethylparamide can be prepared in a pure condition by heating methylamine mellitate for two hours in a sealed tube at 200° and recrystallising the colourless product from chlorobenzene; it is quantitatively hydrolysed to mellitic acid on prolonged boiling with potassium hydroxide solution. D. F. T.

Disulphides with Neighbouring Double Linkings. Derivatives of Dithiobiurets and of Thiurets. EMIL FROMM [and RICHARD HEYDER, ADOLF JUNG, and MARGRET STURM] (*Annalen*, 1912, 394, 258—284).—Since only one example is known of the simultaneous production of an arylguanidoarylthiocarbamide and a diarylguanidothiocarbamide by the decomposition of an arylthiuret by an aromatic amine (A., 1908, i, 700), the action of different aromatic amines on a series of thiurets has been examined. It is found that, as a rule, the two products of the decomposition are formed when the arylthiuret and the aromatic amine contain the same aromatic group.

o-*Anisyldithiobiuret*, $C_9H_{11}ON_3S_2$, m. p. 153°, yellowish-white needles, obtained by heating equal weights of perthiocyanic acid and o-anisidine on the water-bath, is converted by boiling hydrochloric acid and ferric chloride into o-*anisylthiuret hydrochloride*, $C_9H_9ON_3S_2,HCl$, m. p. 220° (hydrated) or 235° (anhydrous). The latter and o-anisidine in

boiling alcohol yield sulphur, o-*anisylguanido*-o-*anisylthiocarbamide*, $OMe\cdot C_6H_4\cdot NH\cdot CS\cdot NH\cdot C(:NH)\cdot NH\cdot C_6H_4\cdot OMe$ (the constitution of which is proved by its conversion into o-*anisylguanido*-o-*anisyl*-ψ-*benzylthiocarbamide*,

$$OMe\cdot C_6H_4\cdot N:C(S\cdot C_7H_7)\cdot NH\cdot C(:NH)\cdot NH\cdot C_6H_4\cdot OMe,$$

m. p. 116°, by boiling with benzyl chloride and an excess of aqueous alcoholic sodium hydroxide), and *di*-o-*anisylguanidothiocarbamide*, which is isolated as the *hydrochloride*,

$$C(NH\cdot C_6H_4\cdot OMe)_2:N\cdot CS\cdot NH_2,HCl,$$

m. p. 205°. By boiling this hydrochloride with lead oxide and alcoholic sodium hydroxide, *di*-o-*anisyldicyanodiamide*,

$$CN\cdot N:C(NH\cdot C_6H_4\cdot OMe)_2,$$

m. p. 168°, white needles, is obtained. In a similar manner, *p*-phenetylthiuret hydrochloride and *p*-phenetidine in boiling alcohol yield *di*-p-*phenetylguanidothiocarbamide*, m. p. 142° (*hydrochloride*, m. p. 167°), and p-*phenetylguanido*-p-*phenetylthiocarbamide*, m. p. 172°, of which the former is converted into *di*-p-*phenetyldicyanodiamide*, m. p. 176°, by lead oxide and alcoholic sodium hydroxide, and the latter into p-*phenetylguanido*-p-*phenetyl*-ψ-*benzylthiocarbamide*, m. p. 180°, by benzyl chloride and alcoholic sodium hydroxide. *p*-Phenetylthiuret hydrochloride and aniline react to form phenylguanido-*p*-phenetylthiocarbamide, m. p. 184°, not 170° (A., 1907, i, 982), and a small amount of *phenyl*-p-*phenetylguanidothiocarbamide*, $OEt\cdot C_6H_4\cdot NH\cdot C(NHPh):N\cdot CS\cdot NH_2$, m. p. 137°, the *hydrochloride* of which, $C_{16}H_{18}ON_4S,HCl,H_2O$, has m. p. 113—114°.

p-Phenetylguanidophenylthiocarbamide (*loc. cit.*) has m. p. 158°, not 168°, and forms a *hydrochloride*, m. p. 168°.

o-*Tolylthiuret hydrochloride*, $C_9H_9N_3S_2,HCl,2H_2O$, m. p. 175°, obtained from *o*-tolyldithiobiuret and boiling hydrochloric acid and ferric chloride, reacts with *o*-toluidine in boiling alcohol to form *tri*-o-*tolyldiguanide hydrochloride*, $C_{23}H_{25}N_5HCl$, m. p. 233°, from which *tri*-o-*tolyldiguanide*, $C(NH\cdot C_6H_4Me)_2:N\cdot C(:NH)\cdot NH\cdot C_6H_4Me$, m. p. 179°, is liberated by ammonia. The by-product of the preceding reaction is *di*-o-*tolylguanidothiocarbamide*, m. p. 172°, or o-*tolylguanido*-o-*tolylthiocarbamide*, $C_{16}H_{18}N_4S,EtOH$, m. p. 178°, according to the dilution of the solution. *o*-Tolylthiuret and aniline in boiling alcohol yield only *phenylguanido*-o-*tolylthiocarbamide*, m. p. 135° (*hydrochloride*, m. p. 183°), and phenylthiuret and *o*-toluidine under similar conditions yield only *phenyl*-o-*tolylguanidothiocarbamide*, m. p. 111° (*hydrochloride*, m. p. 89°). *Phenylguanido*-o-*tolyl*-ψ-*benzylthiocarbamide*, $C_{22}H_{22}N_4S$, m. p. 124°, crystallises in yellow octahedra.

The following substances have been obtained by the interaction of arylthiuret hydrochlorides and phenylhydrazine in boiling alcohol (A., 1907, i, 982; 1908, i, 700), and are converted into triazole derivatives by boiling aqueous alcoholic alkalis; thus *o*-tolylthiuret hydrochloride and phenylhydrazine yield *anilguanido*-o-*tolylthiocarbamide* or *anil*-o-*tolylguanidothiocarbamide*,

$$NHPh\cdot NH\cdot C(:NH)\cdot NH\cdot CS\cdot NH\cdot C_6H_4Me \text{ or}$$

$NHPh\cdot NH\cdot C(NH\cdot C_6H_4Me):N\cdot CS\cdot NH_2$, m. p. 157° [3:5(or 5:3-)-*amino*-o-*toluidino*-1-*phenyltriazole*, $NPh<\begin{matrix}N\!=\!=\!=\!=\!=\!=C\cdot NH_2\\ C(NH\cdot C_6H_4Me):N\end{matrix}$ or

$NPh<\begin{matrix} N{=\!=\!=}C{:}NH{\cdot}C_6H_4Me \\ C(NH_2){:}N \end{matrix}$, has m. p. 143°]; *o*-anisylthiuret and phenylhydrazine yield two substances which could not be obtained pure, but have been converted into 5-*amino-3-o-anisidino-1-phenyltriazole*, $OMe{\cdot}C_6H_4{\cdot}NH{\cdot}C<\begin{matrix} N{\cdot}NPh \\ N{:}C{\cdot}NH_2 \end{matrix}$, and 3-*amino-5-o-anisidino-1-phenyltriazole*, one of which forms a sparingly soluble *hydrochloride*,

$$C_{15}H_{15}ON_5,HCl,H_2O,$$

m. p. 228°, and a *picrate*, m. p. 250°, red needles, and the other an easily soluble *hydrochloride*, and a *picrate*, m. p. 169°; *p*-phenetylthiuret hydrochloride and phenylhydrazine (Fromm and Vetter, A., 1907, i, 982) yield anilguanido-*p*-phenetylthiocarbamide or anil-*p*-phenetylguanidothiocarbamide, m. p. 170°, not 168°, and aminophenylguanido-*p*-phenetylthiocarbamide or aminophenyl-*p*-phenetylguanidothiocarbamide, m. p. 168°, white needles (not m. p. 236°, white leaflets), the latter forming a *benzylidene* derivative, m. p. 183°.

The formation of 3-amino-5-thiol-1-phenyltriazole, m. p. 234°, and dianildithiobiuret, m. p. 178°, from phenylhydrazine and phenylmethylthiuret has already been recorded (A., 1908, i, 700). The former reacts with benzyl chloride and aqueous sodium hydroxide to form 3-*amino-5-benzylthiol-1-phenyltriazole*, m. p. 116°, and with benzoyl chloride and aqueous sodium hydroxide to form 3-*benzoylamino-5-thiol-1-phenyltriazole*, m. p. 267°, from which 3-*benzoylamino-5-benzylthiol-1-phenyltriazole*, m. p. 161°, is obtained by means of benzyl chloride and aqueous sodium hydroxide. The action of benzoyl chloride and sodium carbonate on dianildithiobiuret or on 3-thiol-5-phenylhydrazino-1-phenyltriazole yields 3-*thiol-5-benzoylphenylhydrazino-1-phenyltriazole*, $NHPh{\cdot}NBz{\cdot}C<\begin{matrix} NPh{\cdot}N \\ N{-\!-}C{\cdot}SH \end{matrix}$, m. p. 218°, which yields the 3-*benzylthiol* derivative, m. p. 171°, by boiling with benzyl chloride and the calculated quantity of aqueous alcoholic sodium hydroxide, and 3-*benzylthiol-5-phenylhydrazino-1-phenyltriazole*, m. p. 118°, red needles, when an excess of the alkali is employed. The substance, m. p. 218°, obtained by the action of acetic anhydride on dianildithiobiuret (*loc. cit.*) is 3-*thiol-5-acetylphenylhydrazino-1-phenyltriazole*; by treatment with benzyl chloride and an alkali, it yields 3-*benzylthiol-5-acetylphenylhydrazino-1-phenyltriazole*, m. p. 102°, yellow leaflets. The constitution of the oxidation product, m. p. 218°, of 3-thiol-5-phenylhydrazino-1-phenyltriazole as a benzeneazotriazole (*loc. cit.*) is proved as follows. In the presence of an alkali, the substance is converted into 5-*benzeneazo-3-thion-2-benzoyl-1-phenyltriazole*, $PhN_2{\cdot}C<\begin{matrix} NPh{\cdot}NBz \\ N{-\!-}CS \end{matrix}$, m. p. 167°, red needles, by benzoyl chloride, and into 5-*benzeneazo-3-benzylthiol-1-phenyltriazole*,

$$PhN_2{\cdot}C<\begin{matrix} NPh{\cdot}N \\ N{-\!-}C{\cdot}SC_7H_7 \end{matrix},$$

m. p. 116°, reddish-yellow leaflets, by benzyl chloride. The latter is also produced when the former is treated with benzyl chloride and an alkali. The oxidation product can be acylated or alkylated, but not

both simultaneously, thus proving that the same hydrogen atom is concerned in each process and that the substance is tautomeric.

The base $C_{14}H_{13}N_5S$, m. p. 181°, which is obtained together with the preceding azo-compound by the action of boiling hydrochloric acid on dianildithiobiuret (*loc. cit.*), forms, in addition to the diacetyl and the dibenzylidene derivatives already described, a *dibenzoyl* derivative, m. p. 216°, does not react with benzyl chloride in the presence of an alkali, and requires 2 mols. of sodium nitrite for its diazotisation. These facts are contrary to the formula previously ascribed to the base, and are more in harmony with the constitution:

$$NH_2\cdot C_6H_4\cdot N{:}C{<}{\substack{-S-\\ NH}}{>}C{:}N\cdot C_6H_4\cdot NH_2.$$

Under the influence of hydrogen chloride, substituted dithiobiurets react with aldehydes or ketones to form aldurets or keturets (A, 1893, i, 575; 1906, i, 656), which can be alkylated in consequence of the presence of the thiol groups; thus *o*-tolyldithiobiuret and acetone yield *o-tolyldimethyl-ψ-dithioketuret*, $C_6H_4Me\cdot N{:}C(SH)\cdot N{<}{\substack{C(SH)\\ CMe_2-}}{>}N$, m. p. 236°, which forms a *benzyl* derivative, m. p. 192°, and a *dibenzyl* derivative, m. p. 83°; *o*-tolyldithiobiuret and benzaldehyde yield *phenyl-o-tolyl-ψ-dithioalduret*, $C_6H_4Me\cdot N{:}C(SH)\cdot N{<}{\substack{C(SH)\\ CHPh}}{>}N$, m. p. 207°, yellow leaflets (*dibenzyl* derivative, m. p. 118°); *o*-tolyldithiobiuret and 40% formaldehyde yield *o-tolyl-ψ-dithioalduret*,

$$C_6H_4Me\cdot N{:}C(SH)\cdot N{<}{\substack{C(SH)\\ CH_2-}}{>}N,$$

m. p. 197°, yellow leaflets (*dibenzyl* derivative, m. p. 80°). *o*-Tolyldithiobiuret does not react with acetophenone or benzophenone.

C. S.

Crystallographic Study of the Sodium Salt of *iso*Hydroxytetrazole. Aristide Rosati (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 645—648).—The author has studied the salt $CHON_4Na,3H_2O$, which was obtained by Palazzo (A., 1910, i, 342). The salt loses its water at 120—130°, and explodes at 240°. It occurs in two crystalline forms: (1) pale straw-yellow tablets belonging to the pinacoidal class of the triclinic system; $a:b:c = 1{\cdot}2494:1:0{\cdot}8521$, α 130°6′, β 114°47′, γ 79°34·5′; (2) colourless tablets, also belonging to the pinacoidal class of the triclinic system;

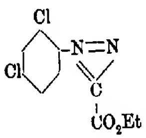
$$a:b:c = 0{\cdot}6798:1:1{\cdot}0834,\ \alpha\ 54°53',\ \beta\ 124°32{\cdot}5',\ \gamma\ 121°43'.$$

R. V. S.

Action of Chlorine on Ethyl Phenylazoacetoacetate. A New Way to Prepare Derivatives of Formimido-chloride. Carl Bülow and Peter Neber (*Ber.*, 1912, 45, 3732—3744).—Elimination of the carbethoxyl group takes place when ethyl phenylazoacetoacetate is hydrolysed by sodium hydroxide (Richter and Münzer, A., 1884, 1342) or brominated (Hecking, *Diss.*, 1910). The action of chlorine, however, results in the removal of the acetyl group and the formation of the dichlorophenylhydrazone of ethyl monochloroglyoxylate. When this substance is completely reduced,

2 : 4-dichloroaniline is formed, and the compound may also be synthesised from this base. The remaining chlorine atom must necessarily be attached to the α-carbon atom of the side-chain, and it is very reactive. It may be replaced by an amino-group, more prolonged action of ammonia replacing, in addition, the ester group.

A method is given for the preparation of ethyl phenylazoaceto-acetate. Chlorination may be effected in glacial acetic acid by chlorine or sulphuryl chloride, but the best results are obtained by chlorine in chloroform. The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-chloroglyoxylate*, $C_6H_3Cl_2{\cdot}NH{\cdot}N{:}CCl{\cdot}CO_2Et$, crystallises in brilliant needles, m. p. 98°. When treated with alcoholic potash, hydrogen chloride is eliminated, and a *product*, $C_{10}H_8O_2N_2Cl_2$, is obtained in beautiful yellow needles, m. p. 196°. Its constitution is probably represented by the annexed formula.



The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-amino-glyoxylate*, $C_{10}H_{11}O_2N_3Cl_2$, which is immediately formed when alcoholic ammonia is added to the imido-chloride, crystallises in long, flat needles from dilute ethyl acetate, m. p. 99°, and is readily soluble in mineral acids, but does not form a diazonium salt. More prolonged action of ammonia results in the formation of the *amide*, $C_6H_3Cl_2{\cdot}NH{\cdot}N{:}C(NH_2){\cdot}CO{\cdot}NH_2$, in long, grey needles, m. p. 170°.

Ethyl 2 : 4-*dichlorobenzeneazoacetoacetate*, $C_6H_3Cl_2{\cdot}N_2{\cdot}CHAc{\cdot}CO_2Et$, may be prepared in a similar manner by condensing the diazotised dichloroaniline with ethyl acetoacetate. It crystallises in yellow needles, m. p. 127°, and gives the above α-chloro-compound with chlorine. When condensed with hydrazine hydrate, it gives 4-o-p-*dichlorobenzeneazo*-5-*hydroxy*-3-*methylpyrazole*, $C_{10}H_8O_2N_2Cl_2$, in orange-yellow needles, m. p. 207°, which cannot be precipitated by water from piperidine, in which the substance is very soluble.

Similarly, phenylhydrazine yields 4-o-p-*dichlorobenzeneazo*-5-*hydroxy*-1-*phenyl*-3-*methylpyrazole*, $C_{16}H_{12}ON_4Cl_2$, in brick-red needles, m. p. 195°, which concentrated nitric acid converts into 2 : 4-dichlorophenyl-diazonium chloride and 4-nitro-1-benzene-3-methylpyrazolone (compare A., 1910, i, 902). J. C. W.

The Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. I. HENRY D. DAKIN (*J. Biol. Chem.*, 1912, 13, 357—362).—There is an analogy between the hydantoin, $NH{<}{\begin{matrix}CO{-}NH\\ CRH{\cdot}CO\end{matrix}}$, and peptide,

$$RCH{<}{\begin{matrix}NH{\cdot}CO{-}\\ CO{\cdot}NH{\cdot}CHR{\cdot}CO_2H\end{matrix}},$$

groupings, in both of which the –CH·CO– group can exhibit keto-enolic tautomerism and hence racemisation (compare Dakin, A., 1910, i, 590). In the peptide complex the terminal amino-acid containing a free carboxyl group cannot, however, undergo this change. Such tautomeric change apparently takes place when a protein is digested at low temperatures with dilute alkali (compare Kossel and Weiss, A., 1909, i, 542; 1910, i, 791).

The optical rotatory power of gelatin falls to a minimum when it is digested with dilute alkali. On subsequent hydrolysis with acids, inactive leucine, aspartic acid, arginine, histidine, and phenylalanine are obtained, whereas proline, glutamic acid, and lysine are obtained in the optically active forms together with part of the alanine. The conclusion is drawn that none of the carboxyl groups in the substances which were obtained inactive are free in gelatin. On the other hand, glutamic acid, lysine, and alanine may have some of their carboxyl groups free, that is, they may occupy terminal positions in the peptide chains. An alternative is that these amino-acids are rapidly liberated in the free state by the hydrolytic action of the alkali and so escape racemisation. E. F. A.

The Refractive Indices of Solutions of Certain Proteins. VIII. Globin. T. Brailsford Robertson (*J. Biol. Chem.*, 1913, **13**, 455—462).—Globin was prepared from ox-corpuscles by three different modifications of Schulz's method. The value of a for the purest preparation dissolved in decinormal potassium hydroxide or hydrochloric acid is $0·00169 \pm 0·00005$. W. D. H.

The Preparation and Properties of a Compound Protein; Globin Caseinate. T. Brailsford Robertson (*J. Biol. Chem.*, 1913, **13**, 499—506).—Globin caseinate may be prepared by mixing two parts of globin with one of casein, each in a faintly alkaline solution. It displays properties intermediate between those of the two component proteins, the acid function of globin being enhanced by union with casein and the basic function of casein by union with globin.

The compound is not decomposed by dilute acetic acid in the cold, but it is by boiling dilute acetic acid, or by pepsin and acetic acid. The change in the refractive index of decinormal potassium hydroxide due to the introduction of 1% of globin caseinate is $0·00162 \pm 0·00005$. The refractivity of a compound protein is an additive function of the refractivities of its components. W. D. H.

Constitution of the Blood and Bile Pigments. I. Hans Fischer and Erich Bartholomäus (*Zeitsch. physiol. Chem.*, 1913, **83**, 50—71).—The formation of tri- and tetra-substituted pyrroles on the decomposition of hæmin is explained on the hypothesis that the pyrrole nuclei are united by a CH_2 radicle in the 2-positions. Such 2- and 3-methylene derivatives have been synthesised by Colacicchi (A., 1912, i, 491).

Bis-(5-acetyl-2 : 4-dimethylpyrryl)methane, in which the methylene group is in the 3-position, resists the reducing action of hydrogen iodide and acetic acid during two hours. To some extent the a-acetyl residue is eliminated and *bis-(2 : 4-dimethylpyrryl-3 : 3')methane*,

$$NH{<}\begin{array}{l}CMe:C-CH_2-C:CMe\\ CH=CMe\quad MeC=CH\end{array}{>}NH,$$

is formed. This compound has many of the properties of hemibilirubin; it gives the aldehyde reaction, is unstable, shows the urobilin bands, and the fluorescence reaction with zinc acetate. It forms a *picrate* and an a-azo-dye.

When the action of the reducing agent is prolonged for fourteen to sixteen hours, 2 : 3 : 4-trimethylpyrrole admixed with some 2 : 4-dimethylpyrrole is obtained.

Bis-(3-acetyl-2 : 4-dimethylpyrryl)methane (Colacicchi, *loc. cit.*) is readily reduced to pyrrole derivatives by acetic acid and hydrogen iodide. The mixture of pyrrole picrates was not separated.

Trialkylated pyrroles condense with formaldehyde in presence of alkali. The products are regarded as methylene derivatives, although the possibility of an alcohol structure, $NH<\begin{matrix}CMe:C\cdot CH_2\cdot OH\\ CMe:CMe\end{matrix}$, is not overlooked.

Tetramethylpyrrole was obtained on reducing the condensation product from 2 : 4 : 5-trimethylpyrrole; phyllopyrrole from the condensation product of cryptopyrrole.

2 : 3 : 5-*Trimethylpyrrole*-4-*propionic acid*,

$$NH<\begin{matrix}CMe:C\cdot CH_2\cdot CH_2\cdot CO_2H\\ CMe:CMe\end{matrix},$$

was not obtained on reducing the amorphous condensation product of formaldehyde with phonopyrrolecarboxylic acid, but it is readily formed on methylation of phonopyrrolecarboxylic acid. Tetramethylpyrrole is obtained at the same time.

The pyrrole, $CO_2Et\cdot C<\begin{matrix}CMe:C-CH_2-C=CMe\\ CMe\cdot NH\qquad NH\cdot CMe\end{matrix}>C\cdot CO_2Et$, obtained by the action of formaldehyde on 3-carbethoxy-2 : 4-dimethylpyrrole, when boiled with acetic acid gives an intense green solution showing a characteristic band in the red similar to that of the copper salt of hemibilirubin.

Bis-5-acetyl-2 : 4-dimethylpyrrylethane,

$$NH<\begin{matrix}CMe=\!=C-CHMe-C=\!=CMe\\ C(COMe):CMe\qquad MeC\cdot C(COMe)\end{matrix}>NH,$$

produced from 5-acetyl-2 : 4-dimethylpyrrole by the action of acetaldehyde, is decomposed by acetic acid and hydrogen iodide into 2 : 4-dimethylpyrrole. The formation of cryptopyrrole could not be determined.

All the foregoing pyrrole derivatives are decomposed by sodium methoxide, forming tetramethylpyrrole.

Tripyrrole is absolutely stable towards acetic acid and hydrogen iodide in the sense that no volatile bases are formed.

Bis-(2 : 4-*dimethylpyrryl*-3 : 3')*methane* crystallises in tiny pyramids and prisms, m. p. 139—140°; the *picrate* forms yellowish-brown needles, m. p. 125—126°.

2 : 3 : 5-*Trimethylpyrrole*-4-*propionic acid* forms a picrate, m. p. 126—127°.
E. F. A.

Bilirubin and Hæmin. William Küster [and P. Deihle] (*Zeitsch. physiol. Chem.*, 1912, 82, 463—483).—Sodium amalgam does not necessarily reduce vinyl groups, which remain unattacked during the conversion of hæmin into the leuco-compound or of bilirubin into hemibilirubin. The complex giving rise to methylethylmaleinimide on oxidation is contained already in bilirubin. One of the two complexes

in hæmin which gives hæmatic acid on oxidation loses carbon dioxide during conversion into bilirubin, and so gives rise to the imide when oxidised. On esterification with methyl alcohol and hydrochloric acid, bilirubin behaves differently from hæmin. A dimethyl derivative is obtained, in which one methyl replaces hydrogen, and the other is due to the addition of methyl alcohol.

The formulæ given by Piloty (A., 1912, i, 923) and by H. Fischer and Röse (A., 1912, i, 575) for bilirubic acid, etc., are discussed, and a complete structural formula for hæmin is suggested.

Pure mesoporphyrin yields methylethylmaleinimide on oxidation.

Bilirubin forms a silver salt containing 4 atoms of silver when fresh preparations are used; older preparations react with 2 atoms only of silver. The salts have a metallic lustre, and the silver is not replaceable by barium. Bilirubin regenerated from the zinc salt dissolves in sodium hydrogen carbonate. This *aci*-form is more soluble in chloroform than the normal. *Dimethylbilirubin*, $C_{34}H_{40}O_7N_4$, is a blackish-green powder. E. F. A.

The Action of Yeast on Yeast-nucleic Acid. SAMUEL AMBERG and WALTER JONES (*J. Biol. Chem.*, 1913, 13, 441—446).—Yeast has no action on thymus-nucleic acid, but it causes the disappearance of yeast-nucleic acid. If compressed yeast is used, adenine and guanine appear; if yeast powder is employed, adenine and guanosine are found. W. D. H.

Nucleases. III. PHŒBUS A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1913, 13, 507—510).—The pyrimidine ribosides are more resistant towards the hydrolytic action of mineral acids than are the purine ribosides. Their behaviour to enzymes runs parallel to this. The differences towards acids can be removed by reducing the pyrimidine base in the riboside to the corresponding dihydropyrimidine. No tissue enzyme has, however, yet been discovered which hydrolyses either the original or the dihydro-derivative.

W. D. H.

Influence of the Reaction of the Medium on the Action of Ptyalin. WILHELM E. RINGER and H. VAN TRIGT (*Zeitsch. physiol. Chem.*, 1912, 82, 484—501).—The action of ptyalin on starch is studied in presence of varying amounts of sodium hydroxide and phosphoric acid, and the amount of reducing sugar formed contrasted with the hydrogen-ion concentration of the liquids as determined by the conductivity method. At 37° the optimum activity is observed in a solution having $p_H = 6{\cdot}0$. When citrate is substituted for phosphate, the position of the optimum varies with the concentration of the citrate; it is observed in more nearly neutral solutions with citrate than is the case with phosphate. In presence of sodium acetate and acetic acid the optimum is at $p_H = 6{\cdot}0$. The presence of both phosphate and acetate reduces the amount of starch hydrolysis; citrate has still more influence. The enzyme itself is not damaged during the duration of the experiment. When these are prolonged for five times as long, the position of the optimum is not materially altered. E. F. A.

Temperatures of Destruction of Emulsin in Ethyl Alcohol of Various Strengths. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 27—31).—A solution of emulsin in water was diluted with alcohol or alcohol and water to produce alcoholic liquids of various strengths containing the same quantity of emulsin. Portions of these liquids were then heated to various temperatures, and afterwards tested for activity on salicin. It was found that the temperature at which emulsin begins to become inactive under these conditions varies from 60° to 40° for liquids containing from 10 to 50% of alcohol, and remains constant at 45° to 40° for liquids containing 60 to 95% of alcohol. Total destruction of activity occurs at temperatures ranging from 70° to 55°. Different figures are obtained when the preparations are made by macerating emulsin in the alcoholic liquids. T. A. H.

Rennin. I. Properties of the Ferment when Prepared by Different Methods. II. Acceleration of the Action of Rennin by Phosphoric Acid. III. The Variation in the Length of Time Required to Curdle Different Specimens of Milk. A. ZIMMERMANN (*J. Ind. Eng. Chem.*, 1912, 4, 506—508).—The distinctive properties of rennin when prepared by the following different methods are described: (1) precipitated by sodium chloride, (2) precipitated by sodium sulphate, (3) rennin in scales (granular rennin), and (4) commercial rennin.

Phosphoric acid (0 075%) when added to milk increases the activity of the rennin, a property possessed in a less degree by lactic, hydrochloric, and oxalic acids.

The length of time required to curdle by the same specimen of rennin appears to be influenced by the length of time the milk has been kept; the staler the milk, the more rapid the action of the rennin; this would appear to be a bacterial effect, yet it is found that a mixture of rennin and milk kept several hours at 40° will not curdle, whereas if the milk alone be subjected to this treatment, the addition of the same rennin causes rapid curdling.

The preparation of standardised rennin, the permanency of rennin solutions and of pepsin are also discussed. F. M. G. M.

Antagonism between Citrates and Calcium Salts in Milk Curdling by Rennet. J. R. KATZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 434—445).—Whilst $N/125$- and $N/25$-solutions of citric acid delay the curdling of milk more than two hours, the action is much weakened when substitution occurs at one of the active groups of the citric acid, and stops altogether when two or three of the groups are made inactive.

When substitution occurs at the alcohol group, the curdling is delayed three and a-half and nine and a-half hours respectively by $N/125$- and $N/25$-solutions. Similar results were obtained by tribasic acids not containing an alcohol group.

When substitution occurs at one carboxyl group in citric acid, a delay in curdling milk of one and a-quarter hours with $N/125$- and of six and a-half hours with $N/25$-solutions takes place. Results similar

to these were again obtained by employing dibasic acids with one or more alcohol groups.

The results show that when one active group is taken from citric acid, the characteristic action of the acid is reduced to about 6% of its original value, and that when two groups are substituted to about 1%.

N. H. J. M.

Synthesising Action between Galactose and Ethyl Alcohol under the Influence of Kephir. Émile Bourquelot and Henri Hérissey *Compt. rend.*, 1912, **155**, 1552—1554).—β-Ethyl galactoside is slowly synthesised, in small quantities in the presence of kephir, from an alcoholic solution of galactose. The authors suggest that the synthesising agent in this case and also in that of emulsin obtained from almonds (compare A., 1912, i, 946) is really the lactase present in these two substances.

W. G.

Physiological Chemistry

Variations in the Irritability of the Reflex Arc. I. Variations under Asphyxial Conditions, with Blood-gas Estimations. E. L. Porter (*Amer. J. Physiol.*, 1913, **31**, 223—244).—The experiments were made on the spinal cat, subjected to asphyxial conditions. The records obtained offer no conclusive evidence of increased reflex irritability under asphyxia, but as the oxygen in the blood lessens and the carbon dioxide accumulates, the flexion reflex disappears. This is the general result, but the details differ according as the admixture of the two gases supplied varies.

W. D. H.

The Chemistry of Portal Blood. I. A Portal Fistula. Efim S. London and N. A. Dobrovolskaja (*Zeitsch. physiol. Chem.*, 1912, **82**, 415—416).—A description of the operative procedure in making a fistula for the obtaining of blood from the portal vein. Results will follow later.

W. D. H.

Glycolysis. III. Peter Rona and F. Arnheim (*Biochem. Zeitsch.* 1913, **48**, 35—49. Compare A., 1911, ii, 619).—The authors confirm the previous statement that sugar is not destroyed by lysed corpuscles. They now show that if the corpuscles are previously lysed, they can still destroy sugar provided that phosphate or carbonate ions are present in sufficient concentration. They further show that the glycolysis is much diminished if intact corpuscles are diluted with physiological saline alone; if, however, carbonates or phosphates are added in sufficient concentration in a Ringer's fluid, when such a liquid is used to dilute the corpuscles, the glycolysis is not less than that produced by the undiluted corpuscles. The comparative glycolytic

properties of white and red corpuscles was also investigated. The red corpuscles diluted with saline to the volume of the original blood exerted nearly as great a glycolytic effect as the original blood, whereas the white corpuscles diluted to the same extent were almost inactive. Nevertheless, if the white corpuscles are diluted with a liquid containing phosphates, they exert a very marked glycolytic action. In the experiments carried out, no glycolytic power markedly superior to that of the red corpuscles could be demonstrated.

S. B. S.

The Alkalinity of Pancreatic and Intestinal Juice in Living Dogs. FRIEDRICH AUERBACH and HANS PICK (*Arb. K. Gesundheitsamte*, 1912, 43, 155—186).—Both these juices are strongly alkaline in spite of the blood being nearly neutral in reaction; the alkalinity was determined in the juices obtained from fistulæ in dogs by electrometric, colorimetric, and titrimetric methods. It corresponds with that of a sodium hydrogen carbonate solution, rather than with one of sodium carbonate. It is probable that the juices contain free carbon dioxide. The H-ion concentration averages $0{\cdot}5.10^{-8}$ mol./litre; the OH-ion concentration at 18° is about 10^{-6}, and at 37°, 5.10^{-6} mol./litre.

In intestinal juice, sodium chloride is more abundant than sodium hydrogen carbonate; in pancreatic juice the reverse obtains. The alkalinity of the duodenal contents corresponds with that which is the optimum for peptolytic (not tryptic) activity. W. D. H.

Effects of Nutrition with Maize. IV. Action of the Succus entericus of the Dog on Zein, Gliadin, Zeoses, and Gliadoses. SILVESTRO BAGLIONI [with G. AMANTEA and L. MANINI] (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 655—660. Compare A., 1911, ii, 999).—The *Succus entericus* of the dog has a weak digestive action on gliadin and an even weaker action on zein, but it has an almost equal digestive action on zeoses and gliadoses of peptic and tryptic origin. R. V. S.

Are the Endogenous Purine Substances the Products of the Activity of the Digestive Organs? FRANZ MAREŠ (*Pflüger's Archiv*, 1912, 149, 275—286).—Polemical against Sivén (A., 1912, ii, 780; compare following abstract). W. D. H.

The Source of Uric Acid in Man. II. FRANZ SMETÁNKA (*Pflüger's Archiv*, 1912, 149, 287—317).—This also is a reply to Sivén's criticism on the work of Mareš (A., 1910, ii, 973) and Smetánka (A., 1911, ii, 218). The article is mainly polemical, but does contain some fresh experimental work, and the main conclusions drawn are as follows. Intake of a purine-free diet causes an increase of purine excretion. This is due to nuclear catabolism occurring in and associated with the activity of the digestive glands. The increase lasts five to six hours after a meal; but when much protein is taken with the evening meal it may go on all night. The question whether variations in the protein intake produce variations in the purine

output is not definitely answered. Diets rich in starch act similarly, but less markedly. The original views of Mareš on the question are considered to remain unshaken. W. D. H.

Animal Calorimetry. VII. The Metabolism of a Dwarf. FRANCIS H. McCRUDDEN and GRAHAM LUSK (*J. Biol. Chem.*, 1913, **13**, 447—454).—A dwarf, suffering from infantilism, seventeen years old, and weighing 21 kilos., had a basal metabolism of 775 calories per square metre of body surface in twenty-four hours; this is about the same as in a dog. The metabolism was increased by 6·6% after food, and this again by 14·7% by reading illustrated periodicals in bed. The protein metabolism yielded the normal proportion of 15% of the total calories of heat-production. Nothing abnormal in metabolic processes was detected. W. D. H.

The Part Played by Acid in Carbohydrate Metabolism. Acid Diabetes. HERBERT ELIAS (*Biochem. Zeitsch.*, 1913, **45**, 120—143).—Relatively small amounts of acids, administered to rabbits, can cause glycogen in large quantities to disappear from the liver; this disappearance results in hyperglycæmia and glycosuria in the animals The fact was established by the distinct positive results obtained in a series of researches in animals with livers rich in glycogen, whereas negative results were obtained from animals in which the livers were glycogen-free. The suprarenals take no part in this action, as positive results were obtained when dyspnœa was avoided, during chloral hydrate narcosis, and after cutting the splanchnics. In all cases, furthermore, the histological structure of the suprarenals remained intact. It was shown also, by perfusion experiments through the isolated liver, that adrenaline plays no part in the disappearance of the glycogen. The acid appears to act, therefore, directly on the liver itself. Perfusion experiments on the isolated liver of tortoises indicated that the glycogen separates from the liver cells for the most part unchanged when acid is added to the perfusion fluid.

S. B. S.

Has Heated Milk the Same Feeding Value as Raw Milk? EICHLOV (*Bied. Zentr.*, 1913, **42**, 56—58; from *Mitt. deut. milchwirt. Ver.*, 1912).—Milk when heated loses the property of being coagulated by rennet, and the soluble calcium salts become insoluble; both changes presumably decrease the feeding value of milk.

Experiments in which dogs (ten days old) were fed for several months with fresh milk and boiled milk respectively gave the following results. The bones of the dogs fed with boiled milk, with one exception, contained less ash than when fed with fresh milk; the blood also contained less ash and only about half as much fibrin as the blood of the dogs which had fresh milk. When milk is heated for ninety minutes in boiling water, ammonia and hydrogen sulphide are produced in small amounts; the vapour from the heated milk also contained phosphorus. N. H. J. M.

The Influence of Standing or Lying on the Metabolism of Cattle. Henry Prentiss Armsby and J. August Fries (*Amer. J. Physiol.*, 1913, 31, 245—253).—Details are given of the increase of metabolism in cattle when they are in a standing as compared with the lying position. The increased emission of heat during the standing periods is accompanied with a correspondingly increased elimination of both carbon dioxide and water. W. D. H.

Nitrogen Retention on Feeding with Urea. Eduard Grafe and K. Turban (*Zeitsch. physiol. Chem.*, 1913, 83, 25—44).—A full account is given of metabolic experiments in dogs and pigs which show that retention of nitrogen occurs when urea is added to a carbohydrate rich diet. Sometimes equilibrium was attained; a small part of the nitrogen was excreted in the after period. W. D. H.

Histochemistry of Spermatozoa. III. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1913, 83, 72—78).—Dried defatted spermatozoa from herrings consists as to three-quarters of nucleic acid and one-quarter of clupeine. The two compounds are united through the free amino-groups of the arginyl groups of the protamine. E. F. A.

The Biochemistry of the Female Genitalia. I. The Lipins (Lipoids) of the Ovary and Corpus Luteum of the Pregnant and Non-pregnant Cow. Jacob Rosenbloom (*J. Biol. Chem.*, 1913, 13, 511—512).—Data are presented showing the percentages of fat, fatty acids, cholesterol, and lipoids in the ovary and corpus luteum of the cow. No increase in these occurs during pregnancy. W. D. H.

The Sulphatide of the Brain. Phœbus A. Levene (*J. Biol. Chem.*, 1913, 13, 463—464).—The lipoid of the brain (ox), which contains sulphur, was isolated from the phosphatides; the method is not described. Elementary analyses are given which differ considerably from those of both Thudichum and W. Koch. W. D. H.

The Influence of Quantity and Concentration of Poisons of the Digitalis Group on the Frog's Heart. Arnold Holste (*Arch. expt. Path. Pharm.*, 1912, 70, 435—438).—The experiments recorded show the importance of concentration as a factor.

W. D. H.

Systole and Diastole of the Heart Under the Influence of Digitalin. Arnold Holste (*Arch. expt. Path. Pharm.*, 1912, 70, 439—446).—It is stated that digitalin applied internally to the heart produces systolic standstill, and to the exterior, diastolic standstill. This has been explained by supposing that the outer layers of the cardiac muscle respond differently to the drug from the internal layers. The present experiments show that the medium used is a factor. Fluids which contain blood, or Albanese's solution, always produce stoppage in systole, whereas if Ringer's solution is employed as the medium, the stoppage is diastolic. W. D. H.

Replacement of Urea in Artificial Solutions for the Isolated Heart of Selachians. R. Bompiani (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 667—672).—Solutions containing urea, when administered by perfusion or otherwise, increase the time of survival of isolated hearts. The author's experiments on isolated hearts of *Torpedo ocellata* and *Scyllium* show that no substance will quite replace urea in this respect, but the derivatives of urea favour the survival more than other substances (methylcarbamide, survival 480 minutes; urea, survival 600 minutes), but the action is less marked the more distantly the substances are related to urea. Neither glycerol, acetone and urethane (although they are soluble in lipoids), nor the amino-acids, glycine, asparagine, aspartic acid and its salts keep the isolated hearts alive. R. V. S.

Toxicological Investigations on Bio-electric Currents. III. Comparative Toxicological Specificity of the Chemical Alteration Current, and Comparative Physiology and Toxicology of the Heart of Helix pomatia. C. Lovatt Evans (*Zeitsch. Biol.*, 1912, 59, 397—414).—Henze and Hermann have shown that skeletal and heart muscle of the frog responds specifically to poisons, and that the electrical changes run parallel to such action. This thesis is supported by the present investigations on the snail's heart, which is recommended as a convenient object for such work. Its electrogram is very simple, showing a pure diphasic effect, which corresponds with the single peristaltic wave which travels over it. Carbon dioxide acts tonically on it. The heart of the snail is sensitive to potassium, and very resistant to calcium; muscarine has the usual effect, but this is not antagonised by atropine. Antiarin has no action, but strophanthin and saponin are active. W. D. H.

Tolerance for Sugar in the Pig. Anton J. Carlson and F. M. Drennan (*J. Biol. Chem.*, 1913, 13, 465—468).—Minkowski stated that the removal of the pancreas in the pig did not result in as severe diabetes as in other animals. In the present experiments, fatal diabetes did occur, but it was of slow onset. The pig has a lower tolerance for dextrose than any species so far studied; that is, it becomes glycosuric when quite small amounts of sugar are given by the mouth.

Occurrence of Metals in the Human Liver. Leopold van Itallie and J. J. van Eck (*Pharm. Weekblad*, 1912, 49, 1157—1163.* Compare Lehmann, A., 1896, ii, 486).—An investigation of the corpses of persons of various ages indicates that arsenic is not a normal constituent of the human liver, but that copper and zinc are always present, the proportion of copper being greater during the fœtal period than in later life. Otherwise, age, sex, occupation, and place of residence appear to have no influence on the proportion of copper and zinc. The values given by Lehmann for the amount of copper present are appreciably too low. A. J. W.

* and *Arch. Pharm.*, 1913, 251, 50—55.

The Influence of Iodine on Autolysis. M. KASCHIWABARA (*Zeitsch. physiol. Chem.*, 1912, **82**, 425—438).—Contrary to the statements of Kepinov (A., 1912, ii, 69), autolysis does not occur in a medium containing 0·5% of sodium hydroxide; what does occur there is hydrolysis produced by the alkali; this is only slightly increased by the presence of iodine. In alkali-free mixtures, iodine increases autolysis only in a slight degree. In rabbits which had received an intravenous injection of Lugol's solution, autolysis of the liver is also slightly accelerated, but even the fresh liver of such animals show an increase in non-coagulable nitrogen. W. D. H.

The Catalytic Action of Iron Salts on the Autolysis of the Liver. LUIGI POLLINI (*Biochem. Zeitsch.*, 1912, **47**, 396—404).—Small and large quantities of ferric sulphate and ferric chloride increase the total nitrogen and the nitrogen of the monoamino-acids, proteoses and purine substances in the autolysis products when calves' liver is allowed to autolyse in the presence of these salts. Small quantities of iron citrate exert a weak inhibitory action, whereas larger quantities exert an accelerating action; still larger quantities inhibit the autolysis as regards total nitrogen and the nitrogen of amino-acids. The proteose nitrogen, on the other hand, continually increases with increasing amounts of the iron salt. Very small quantities of iron lactate accelerate the autolysis, but progressingly larger quantities exert a progressive amount of inhibition. S. B. S.

The Physiology of the Thyroid Glands. The Content of Phosphorus, Nitrogen, and Lipoids in the Organs of Thyroidectomised Animals. A. S. JUSCHTSCHENKO (*Biochem. Zeitsch.*, 1913, **48**, 64—85).—The experiments were carried out with young dogs, of which a certain number were submitted to thyroidectomy, and an equal number from the same litter were used as controls. It was found that the organic and total phosphorus was diminished in the thyroidectomised animals in the brain, heart, and spleen, whereas the inorganic phosphorus is increased. In the liver, the changes were similar, but in the muscles the results were indefinite. In the kidneys the amount of phosphorus in all forms, and especially the inorganic, was increased. The nitrogen in the majority of the organs of thyroidectomised animals was increased; this statement does not apply, however, to the kidneys and the serum. In animals with hyperthyroidism the total and organic phosphorus in brain, muscles, and heart are diminished; in the liver, kidneys, spleen, and serum, on the other hand, they are increased. In most organs, the nitrogen content is diminished. In thyroidectomised animals, the lipoids, and all the fractions of the same, are diminished in quantity in the brain, liver, and muscles, whereas they are in increased amount in the serum. In other organs, the lipoid quantity is also less than in the normal. In hyperthyroidism, the content of lipoid in the serum is diminished, whereas no very definite results were obtained by the examination of other organs. The ratios of the nitrogen to phosphorus in various fractions of the lipoids in thyroidectomised animals, and in cases of hyperthyroidism, were also investigated. Thyroidectomy also

causes increase in the content of the purine substances of the organs. Complete thyroidectomy causes at first an increase in the phosphorus : nitrogen ratio in the urine, followed by a diminution of this ratio; the quantity of urea diminishes. The quantity of ammonia at first falls, and then rises; there is apparently an increase in amino-acids and purine bases; the creatinine, on the other hand, diminishes.

S. B. S.

Seasonal Variation in the Iodine Content of the Thyroid Gland. Atherton Seidell and Frederic Fenger (*J. Biol. Chem.*, 1913, **13**, 517—526).—In sheep, ox, and pig there is about three times as much iodine in the thyroid between June and November as between December and May. In the sheep and ox (but not in the pig) the gland is larger during the latter months. W. D. H.

Enzyme Synthesis. IV. Lactase of the Mammary Gland. Harold C. Bradley (*J. Biol. Chem.*, 1913, **13**, 431—440).—These experiments give no support at all to the theory of enzyme syntheses in tissues, for lactase was never found in the mammary gland, or in the milk. W. D. H.

Muscle Chemistry. IV. The Extractive Nitrogen and the Free Amino-nitrogen, Titratable by Formaldehyde in the Musculature of Different Animals. Giuseppe Buglia and A. Costantino (*Zeitsch. physiol. Chem.*, 1912, **82**, 439—462. Compare A., 1912, ii, 1077, 1078).—A large number of details of the distribution of nitrogen in muscle in many animals are given, and great variations are met with in both vertebrate and invertebrate animals; but no constant and characteristic features distinguish the musculature of the various animal groups. W. D. H.

Muscle Chemistry. V. Purine Bases of the Smooth Muscle of the Higher Animals. Giuseppe Buglia and A. Costantino (*Zeitsch. physiol. Chem.*, 1913, **83**, 45—49).—The purine bases of the smooth muscle of the ox (retractor penis) consist of oxypurines; xanthine, probably preformed, exceeds hypoxanthine in amount, which is the opposite to that found in striated muscle. W. D. H.

The Formation of Lactic Acid in the Antiseptic Autolysis of Organs. Nicolaus Sobolev (*Biochem. Zeitsch.*, 1912, **47**, 367—373).—In estimating the lactic acid produced by autolysis of the organs, account was taken of the amount of acid carried down by the coagulum when the autolysis product was heated, the amount withdrawn from the solution in this process being estimated by Mondschein's method. At the ordinary temperature, less lactic acid is formed on autolysis than at 40°. Most organs show a maximum production at this temperature after about thirty-three days, after which the amount diminishes. The maximum production took place in the liver, followed by the spleen, heart, muscles, and kidneys in diminishing order.

S. B. S.

Enzyme Synthesis. II. Diastase and Glycogen of Animal Tissues. Harold C. Bradley and E. Kellersberger (*J. Biol. Chem.*, 1913, **13**, 419—424).—Tissues rich in diastase may or may not

contain glycogen, and what is more significant from the point of view of the enzyme-synthesis theory, tissues rich in glycogen may or may not contain diastase. W. D. H.

Enzyme Synthesis. I. Lipase and Fat of Animal Tissues. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1913, **13**, 407—418).—No broad correlation exists between the amounts of fat and lipase in tissues. Some of the tissues which actively produce fat may, in fact, contain relatively little lipase, and tissues which are poor in fat may contain a good deal. The experiments afford no support to the theory of enzyme synthesis. W. D. H.

The Influence of the Lipoids on the Action of Oxydases. HORACE M. VERNON (*Biochem. Zeitsch.*, 1912, **47**, 374—395).—If minced tissue is left for half an hour in varying strengths of solutions of a narcotic up to a certain concentration, the narcotic is then washed out and the oxidising power of the tissue tested by α-naphthol and *p*-phenylenediamine, it will be found that the oxidising power is either uninfluenced or increased. In higher concentrations the oxydase is injured. Concentrations, twice or three times as large as those necessary to produce initial action, destroy the oxydase completely, thus, for example, acetone first in 4*M*-solution attacks the oxydase, which is destroyed completely in 7*M*-solution. These limits were investigated in several cases. The concentrations of monohydroxy-alcohols, which degrade the oxidative capacity 50%, are about twenty times stronger than those necessary to narcotise tadpoles, whereas in the case of fatty esters and methylurethane, they are twelve times stronger. In poisons other than lipoid-soluble substances, such as formaldehyde, the range of action is larger; thus, 1330 times as much formaldehyde is necessary completely to destroy the oxydase as is necessary to produce the initial action. In the case of the typical narcotic, paracetaldehyde, the relationship of these quantities is only 1·8 : 1. The range of action of ammonia is even greater than that of formaldehyde. Concentrations of narcotics which cause the initial effects are only a little greater than those necessary to hæmolyse red blood-corpuscles. The author draws the conclusion that the action of the indophenol oxydase is dependent on the lipoid, or perhaps the lipoid membrane, which, he considers, holds together the tissue oxydase and the peroxydase, which are thereby enabled to exert their joint action. S. B. S.

The Ferments of the Purine Group. ARTHUR SCHULZ (*Biochem. Zeitsch.*, 1913, **48**, 86—119).—In estimating uric acid in organs, formaldehyde up to 2% was added to the solution, after coagulating the proteins in the presence of sodium chloride and acetic acid. The effect of this addition is to render the uric acid more soluble. It was then estimated in the filtrate in the ordinary way by the Schmid-Krüger method. For investigating the uricolytic ferment, dried organ powders were generally employed. It was found that radium emanations of an activity of 5—10 Mache units per c.c were without any recognisable influence on the uricolytic action of

dogs' liver or ox-kidneys. Radium emanations increase the activity of the uricolytic ferments of ox-spleen, both as regards the formation of uric acid from added purine bases and from those produced by autolysis. The increased amount of uric acid formed varied, under the conditions of the experiments, from 10 to 20%. There was an increase, in the case of autolysis, in the activity of the proteolytic ferments, as shown by the increase in the nitrogen of the uncoagulable substances. This amount was, however, relatively less than the increased amount of uric acid formed. The uricolytic ferments of ox-kidneys are totally inhibited in action by fresh pulp of ox-spleen. Ox-kidney powder can inhibit the purine deamidases and the oxydases of the ox-spleen, but not the autolytic uric acid formation by the same organ. The author did not succeed in producing anti-uricolytic ferments by immunisation of rabbits by organs containing uricolytic ferments. S. B. S.

Creatine, Creatinine, and Monoamino-acids in Certain Fishes, Mollusca, and Crustacea. Y. OKUDA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, **5**, 25—31).—Seven varieties of fishes were found to contain from 0·421 to 0·754% of creatine and 0·070 to 0·660% of creatinine. Mollusca contained only traces of these compounds, and crustacea only traces, if any at all.

All the marine animals examined contained much more nitrogen as organic bases than in the form of monoamino-acids, the amount of which is usually very small in fish, but somewhat higher in lobsters and cuttle-fish.

Most of the proteins are soluble in dilute alkali solution, and a good deal is soluble in 10% sodium chloride. N. H. J. M.

The Occurrence of Glycogen in Sea-Molluscs (Especially Cephalopods and Aplysiæ). EMIL STARKENSTEIN and MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1912, **82**, 417—424).—*Cephalopods* and *Aplysiae* have been stated to be free from glycogen. This is not so; they contain abundance of it. Glycogen is the same substance whether it is derived from vertebrates or invertebrates. W. D. H.

Carbon Metabolism. The Labile and Stable Carbon of the Urine. ENRICO REALE (*Biochem. Zeitsch.*, 1912, **47**, 355—366).—The carbon of the urine was estimated by a wet-oxidation process, by oxidation with chromic acid and sulphuric acid, for which a modification of the apparatus of Desgrez (which is figured in the text) was employed. It was found that only about half the carbon in the urine exists in the form of urea. It was also found that a part of the carbon is readily oxidised to carbon dioxide in the presence of hydrogen peroxide when manganese peroxide is used as a catalyst. This is designated by the author "labile carbon," whereas the carbon which is not so oxidised is called "stable carbon." Full experimental details for the estimation of carbon in these two forms are given. S. B. S.

The Intensity of Urinary Acidity in Normal and Pathological Conditions. LAWRENCE J. HENDERSON and WALTER W. PALMER (*J. Biol. Chem.*, 1913, **13**, 393—405).—Normal urine ranges

from a concentration of ionised hydrogen of about 4·82 to 7·45; the mean value is 6·00. Pathological conditions occasionally cause a greater acidity, but never unusual alkalinity. No attempt is made at present to generalise, except in cases of cardio-renal disease, where the high mean acidity may indicate a form of acidosis. W. D. H.

The Origin and Destiny of Cholesterol in the Animal Organism. X. The Excretion of Cholesterol in Man when Fed on Various Diets. GEORGE W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1912, *B*, 86, 13—18. See A., 1912, ii, 275, 958).—In man as in other animals, the excretion of cholesterol in the fæces can be accounted for by that taken in with the food, provided the body-weight remains constant. If, however, a rapid loss of weight takes place, as in illness, the output of cholesterol exceeds the intake.

Further work will be necessary before this view can be regarded as established. W. D. H.

Influence of Alkaline Salts in the Elimination of Urinary Ammonia by Normal Dogs. HENRI LABBÉ (*Compt. rend.*, 1912, 155, 1620—1622. Compare A., 1911, ii, 220).—With dogs in a state of nitrogenous equilibrium on a meat diet, the simultaneous ingestion of ammonium salts and excess of sodium carbonate produces a slightly less elevated elimination of volatile basic nitrogen than when the ammonium salts are ingested alone. The difference is more marked with ammonium carbonate than with ammonium chloride. A large excess of sodium carbonate (about 2 grams per kilo. of body-weight), which provoked great thirst and marked polyuria, did not cause all the basic volatile nitrogen to disappear. W. G.

The Relationship between the Nitrogen of the Amino-acids and Total Nitrogen in Urine under Various Normal and Pathological Conditions. ERNESTO SIGNORELLI (*Biochem. Zeitsch.*, 1912, 42, 482—506).—The experiments were carried out on dogs. The percentage of the amino-acid nitrogen (of the total nitrogen) varied in starvation between 1·09 and 1·30. It showed no very marked increase when oxidation was increased by the animals breathing pure oxygen. The value showed no marked differences when the proteins ingested by the animals were varied (caseinogen, gelatin, gluten, and zein). The percentage was only slightly increased (1·57—2·51) when the hydrolysis products of these proteins were administered subcutaneously. When azoturia was produced by fever, etc., the percentage still remained normal. In phosphorus poisoning, when the functions of the liver were disturbed, it rose to 3·66. Two hypotheses are advanced to account for the approximate constancy of the percentage: (*a*) that in all proteins there is a part which is not readily oxidised, and (*b*) that in the enzyme reaction producing deamidisation there is an equilibrium point at which part of the substance remains unacted on. S. B. S.

The Fat Content of Normal and Pathological Urine. KŌZŌ SAKAGUCHI (*Biochem. Zeitsch.*, 1913, 48, 1—34).—The method

employed for estimating fat was that of Kakiuchi (A., 1910, ii, 549). The amount excreted in a normal adult urine is 0·0085 gram in twenty-four hours, which can be increased to 0·0341 gram after diets containing very large amounts of fat. Out of three cases of nephritis investigated, in only one was the fat excretion regularly above normal. In diabetes, tuberculosis of the lungs, jaundice, and cirrhosis of the liver, the excretion was normal. No extra excretion could be detected in cases of fractures of bones or re-section, and in this respect the results of the author differ from those obtained by earlier investigators. S. B. S.

Urobilin. III. and IV. G. FROMHOLDT and N. NERSESSOV (*Chem. Zentr.*, 1912, ii, 1678; from *Zeitsch., expt. Path. Ther.*, 1912, 11, 400—407).—The administration of fresh bile leads to the appearance of urobilin in the urine, but this does not occur when pure bilirubin or bile extracted with ether is given. A method of extracting urobilin from blood is described. After preliminary extraction with alcohol and filtration, it is acidified and extracted with amyl alcohol, in which solvent the pigment is detected spectroscopically. If urobilin is absent from the urine, it is also absent from the blood, but when present in the urine it is usually present in the blood as well. W. D. H.

Blood Destruction, Bile and Urobilin. The Formation of Bile Pigment in Blood. III. THEODOR BRUGSCH and KARL RETZLAFF (*Chem. Zentr.*, 1912, ii, 1678—1679; from *Zeitsch. expt. Path. Ther.*, 1912, 11, 508—525).—Estimations of urobilin in urine and fæces in various cases of liver disease lead to the conclusion that urobilinuria is the clinical expression for a series of substances related to blood and bile pigment. Hæmatogenous or extra-hepatic urobilinuria occurs after extravasation of blood in the tissues; its other cause is usually hepatic insufficiency. If the bile enters the intestine, its pigment is converted into urobilin and re-absorbed; the liver then manifests its insufficiency by being incapable of re-synthesising bile-pigment from the urobilin, which therefore passes into the blood and urine. Urobilin in urine and fæces was estimated by making alkaline with ammonium carbonate and letting the mixture remain at 37° for two days. It was then extracted with light petroleum until Ehrlich's reaction was negative, then acidified with tartaric acid, and extracted with ether. A measured quantity of the ethereal solution was mixed with an ethereal solution of *p*-dimethylaminobenzaldehyde and a few drops of hydrochloric acid in absolute alcohol, and examined chromophotometrically. W. D. H.

The Protective and Curative Properties of Certain Foodstuffs against Polyneuritis Induced in Birds by a Diet of Polished Rice. EVELYN A. COOPER (*J. Hygiene*, 1913, 12, 436—462).—In pigeons weighing 350 grams, as much as 20 grams of raw beef are necessary daily to prevent polyneuritis; the anti-neuritic value of beef is therefore low. Heart muscle is better, and sheep's brain about twice as efficient as beef. Brain is specially efficient in preventing loss of body-weight which ensues when polished

rice is given. Fish is very inefficient in both directions. Egg-yolk, even if boiled, is the most efficient of all the animal foods examined: 3 grams daily is enough. Dried lentils and unhusked barley are about equal to egg-yolk. Yeast is the most efficient of all foods. The antineuritic and weight-maintaining action of the various foods differs. The weight-maintaining constituents are not protein, fatty or lipoidal. W. D. H.

Congenital Family Steatorrhœa ARCHIBALD E. GARROD and W. H. HURTLEY (*Quart. J. Med.*, 1913, **6**, 242—258).—The details of a curious case of an inborn metabolic error are recorded. The boy (aet. 8) has been subject since infancy to the passage of liquid fat from the bowel; one cooling it solidifies; another brother who died in infancy had the same defect. Health was apparently unaffected; the stools contained 25% of the fat in the food; with an intake of 177 grams of fat only 4% was split; this figure rises when the intake is less, but even then it is not absorbed. Sodium glycocholate and various pancreatic preparations increased fat-splitting, but not the absorption; indeed, the latter aggravated the condition. W. D. H.

The Mechanism of the Action of Silver Haloids. OSKAR GROS (*Arch. expt. Path. Pharm*, 1912, **70**, 375—406).—Colloidal silver chloride and iodide intravenously injected in rabbits are strongly toxic, and the chloride is more so, even though the concentration of silver ions is the same in both cases. This is considered to be due to the formation of a complex of the silver salt and the chlorides of the blood plasma which is more readily carried to the tissue cells. Sodium iodide, which is non-toxic if given simultaneously, increases the poisonous action of silver iodide. This is explained on similar lines. In vitro, both salts are hæmolytic, and again the chloride is more effective, but here sodium iodide does not increase the action of silver iodide. W. D. H.

A Physiological Series of Cations. N. K. KOLTZOV (*Pflüger's Archiv*, 1912, **149**, 327—363).—The observations were made on the effect of salt solutions on the vitality and contractility of a marine infusorian (*Zoothamnium alternans*). They follow in the main the work of Overton and others who have bestowed attention to osmotic phenomena and the rôle of the plasmatic membrane of cells. If chlorides are employed throughout, the cations are arranged in the following order: K, Rb, Na, Cs, NH_4, Li, Sr, Mg, and Ca. Each member of the series lowers the surface tension of plasma-water less than the succeeding one, and toxicity runs parallel with the adsorption of the cations. W. D. H.

Temporary Fixation and Mode of Elimination of Manganese in the Rabbit. GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Compt. rend.*, 1912, **155**, 1556—1559).—Four rabbits received repeated subcutaneous injections of manganous sulphate in varying doses, and the effect on their weight and length of life was noted.

Even with minute doses there was a marked loss in weight, and three injections of 5 mg. of manganese per kilo. of body-weight, at intervals of twenty-four hours, caused the death of the rabbit. The amount of manganese in the various organs of the four rabbits and of an uninjected rabbit was determined, and the results show that manganese, when subcutaneously injected, is rapidly diffused throughout the body, and all the tissues, including the nervous tissue, become temporarily impregnated. It is readily eliminated through the liver, bile, and mucus of the alimentary canal, and a small quantity is excreted in the urine. W. G.

The Action of Certain Substances of the Chloroform Group on the Vestibular Eye-Reflex. J. Rothfeld (*Pflüger's Archiv*, 1913, **149**, 435—446).—Nystagmus (vestibular eye-reflex) disappears under the influence of narcotics; first vertical, then rotatory, and finally horizontal nystagmus. As anæsthesia passes off, they reappear in the reverse order. The substances employed in the research were chloroform, ether, chloral hydrate, and paracetaldehyde. The differences in detail between these four substances are treated at length. W. D. H.

The Fixation of Digitoxin (Merck) in the Organism of the Rabbit after Intravenous Injection. Comparative Experiments with Strophantin-*g*. Camill Lhoták von Lhota (*Biochem. Zeitsch.*, 1913, **48**, 144—154).—If digitoxin is injected intravenously into rabbits, it disappears almost immediately from the blood (as ascertained by tests on the frog's heart), even when ten times the lethal dose is employed and the conditions of the animal are favourable. These conditions are, that the heart should be active, and the functions of the blood-vessels intact. If these are interfered with in any way (by narcosis, etc.), digitoxin can be detected in the blood when only twice the lethal dose has been employed. After injection of ten lethal doses, the digitoxin can be detected in all organs, especially the heart and liver. The greater the length of the circulatory system the drug must travel from the point of injection to reach the heart, the greater is the dose necessary to produce the specific action. This fact indicates that the drug is fixed by the vessels as well as the heart, and was demonstrated by experiments on animals with crossed circulatory systems. The drug can also be detected chemically at the point of application. Intravenously injected strophantin-*g* only disappears immediately from the blood in small quantities. S. B. S.

The Fate of Proline in the Animal Body. Henry D. Dakin (*J. Biol. Chem.*, 1913, **13**, 513—516).—When proline is added to blood, and the mixture perfused through the surviving liver of a dog, there is no increase in the formation of acetoacetic acid; but in the glycosuric animal it causes a marked increase in the sugar output. The formation of dextrose from proline involves the disruption of the ring. Glutamic acid also yields sugar (Lusk); so also do arginine and ornithine. The close structural relationship of glutamic acid, ornithine, and proline is shown graphically. W. D. H.

The Results of Poisoning with Adrenaline, Histamine, Pituitrin and Peptone in Relation to Anaphylaxis and the Vegetative Nervous System. ALFRED FRÖHLICH and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1912, 71, 23—61).—The substances mentioned in the title greatly lessen or abolish the excitability of the autonomic nervous system, both to faradic stimuli and to drugs. The same occurs in "peptone immunity" and in anti-anaphylaxis. As both these phenomena soon disappear, they are separable and reversible. The effect of the poisons is a selective one on the nerve endings. A considerable amount of the work recorded was performed on the uterus, and it was then found that after the use of histamine, adrenaline and pilocarpine had no effect, and pituitrin very little. After treatment with tyramine, pituitrin, histamine and adrenaline act normally; after treatment with pituitrin, adrenaline acts normally; after peptone, pituitrin, tyramine and adrenaline have no action. Barium chloride locally applied to the uterus causes contraction of the uterus after it has been rendered inexcitable by histamine, tyramine, or peptone. W. D. H.

The Pharmacological Action of *p*-Hydroxyphenylethylamine. A. BICKEL and MICH. PAVLOV (*Biochem. Zeitsch.*, 1912, 47, 345—354).—This substance, which can be isolated from ergot, shows the following actions. When 1—2 c.c. of a 0·5% solution are injected into rabbits or dogs of medium size, the arterial blood-pressure, after a short-lasting fall, rises, remains high for two or three minutes, and then sinks to normal. This is due to a contraction of the capillaries, with a consequent diminution of the amount of blood in the veins, which was detected by the measurement of the blood-flow in the venous system. As a further consequence there is a diminution of volume of organs which have a well-developed venous supply. This fact was demonstrated directly by the measurement of changes produced in the kidneys after the injection of the drug, and indirectly by the changes in the intestinal volume after injection of extracts of *Secale cornutum*. S. B. S.

Action of Scopolamine (Hyoscine). ARTHUR R. CUSHNY (*Arch. expt. Path. Pharm.*, 1912, 70, 433—434).—A criticism on the work of Hug (A., 1912, ii, 790), who finds, like the author, that *l*- and *i*-hyoscine differ in their action on nerves. The quantitative differences between the two workers are explained as due to differences in the methods used. W. D. H.

The Method of Action of Quinine. J. MOLDOVAN (*Biochem. Zeitsch.*, 1912, 47, 421—446).—The action on *Colipidia* is to cause a change in the state of the colloids of the protoplasm, leading to a separation of droplets of lipoid character, and producing a change in the osmotic relationship of the protoplasm to its surroundings; afterwards the nucleus and motility of the cell are injured, and finally death results. The cause of death is the stoppage of oxygen respiration. In the case of trypanosomes, the action is similar, but the separation of droplets is less marked, owing to the smaller content of lipoids. Similar actions were also observed on plant cells. There is a con-

siderable difference of behaviour in the individual cells as regards the resistance to the action of quinine, which depends on the energy of the oxygen respirations; older cells appear to be more resistant than young cells. The combined effect of two toxins on the cells is not the sum of the effect of each individual toxin, but depends, amongst other factors, on the relative concentrations of the two. In rabbits and guinea-pigs, the action of quinine is to diminish the oxidative processes, especially in the brain. This fact was demonstrated by various methods of intra vitam staining (according to the method of Ehrlich, etc.). The quinine in influencing the oxidative process does not effect the oxygen taken up, but acts as an anticatalyst. In view of the first action of quinine on cells, in causing the separation of the lipoids, it can act as a narcotic or local anæsthetic. To produce general narcosis, however, the required dose is so high that it acts deleteriously on the respiration, and it cannot therefore be used in practice for this purpose. S. B. S.

Influence of the Constitution of Purine Derivatives on their Action with Respect to Arterial Pressure. Alexandre Desgrez and Dorléans (*Compt. rend.*, 1913, **156**, 93—94).—Whilst guanine on intravenous injection into a rabbit causes a diminution in the arterial blood pressure (compare A., 1912, ii, 585), hypoxanthine, xanthine, and uric acid exert a hypertensive action. The increase in pressure, whilst slight for hypoxanthine, is greater for xanthine and still greater for uric acid. From this it appears that the guanine owes its hypotensive action to the presence of the amino-group in its molecule. The action of these substances, especially of uric acid, is of interest in the pathogenesis of arthritic diseases, in which Bouchard has shown that there is marked arterial hypertension. W. G.

The Biological Action of Certain Protein Products Introduced Parenterally. Alfred Schittenhelm and Wolfgang Weichardt (*Chem. Zentr.*, 1912, ii, 1680; from *Zeitsch. Immunitäts-forsch. exper. Ther.*, 1912, **14**, 609—630).—The simple and conjugated proteins introduced into the blood stream are relatively innocuous; but the protein constituents of conjugated proteins (globin, histone, protamine) cause great depression of blood pressure, affect breathing and temperature, and lead in quite small doses to death. This has been attributed to the high percentage of diamino-acids they contain, but this cannot be the case because histone is poor in such acids, and certain kyrines rich in them are not toxic. Such proteins when united to nucleic acid or to hæmochromogen in the case of globin lose their toxicity. Toxic symptoms which occur when hæmolysis takes place in the blood stream may be due to the liberation of the poisonous globin (proteinogenous cachexia). W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Relation of Concentration of Food-supply to the Generation Time of Bacteria. W. J. PENFOLD and (Mrs.) DOROTHY NORRIS (*J. Hygiene,* 1913, **12**, 527—531).—The generation time of *B. typhosus* in 1% peptone at 37° is forty minutes. If the peptone solution is less than 0·2% in strength the generation time is inversely proportional to the concentration. The addition of 0·17% of dextrose to a medium containing only 0·1% of peptone lowers the generation time by 50%; with 1% peptone this effect is less marked.

W. D. H.

The Bactericidal Properties of Blood Serum. I. The Reaction Velocity of the Germicidal Action of Normal Rabbit Serum on the Bacillus coli commune, and the Influence of Temperature Thereon. (Miss) HARRIETTE CHICK (*J. Hygiene,* 1913, **12**, 414—535).—The action *in vitro* of rabbit serum on *B. coli* consists of several phases, the duration of which is inversely proportional to temperature. Its germicidal action follows the logarithmic law, and so falls into line with other cases of disinfection. Its temperature-coefficient is low (2·84 to 1·93). W. D. H.

Chemical Action of Bacillus cloacæ (Jordan) on Citric and Malic Acids. JAMES THOMPSON (*Proc. Roy. Soc.,* 1912, *B*, 86, 1—12).—The respiratory coefficient for malic and citric acids was determined and found to be 1·63 and 2·35—3 2 respectively.

In the presence of oxygen, *B. cloacæ* decomposes malic acid with the production of carbon dioxide, acetic acid, succinic acid, a small quantity of fatty substance, and traces of alcohol. It is suggested that the action probably goes on in two ways: an oxidation of acid to carbon dioxide and acetic acid by atmospheric oxygen, and an oxidation accompanied by reduction of a portion of the acid to succinic acid. The organism does not attack malic acid in the absence of oxygen.

The products resulting from the decomposition of citric acid are the same as from malic acid. Under aerobic conditions the amount of acetic acid is greater, whilst anaerobic conditions lead to an increase in the production of acetic and formic acids. Acetylmethylcarbinol is not formed by the action of *B. cloacæ* on malic or citric acids.

H. B. H.

The Degradation of Polypeptides by Bacteria. II. The Action of the Non-liquefying Organisms TAKAOKI SASAKI (*Biochem. Zeitsch.,* 1912, **42**, 462—471. Compare A., 1912, ii, 669).—Organisms which are incapable of liquefying gelatin contain nevertheless an erepsin-like ferment capable of hydrolysing glycyl-glycine and glycyl-*l*-tyrosine. Relatively large quantities of tyrosine could be isolated as a result of the action. This action was demonstrated

by typhus and various strains of paratyphus bacilli, various bacilli of dysentery, bacilli of mouse typhus, chicken cholera, and *Micrococcus tetragenus*. S. B. S.

The Degradation of Polypeptides by Bacteria. III. The Action of Liquefying Organisms. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1912, **47**, 472—481).—Glycyl-glycine and glycyl-*l*-tyrosine were hydrolysed (in Fränkel's solution) by the following strains. Bacilli of splenic fever, *Staphylococcus pyogenes aureus*, *citreus*, and *albus*, *B. subtilis*, *B. proteus vulgaris*, *B. pyocyaneus*, *B. prodigiosus*, cholera vibrio, and the vibrios of Metchnikov and Dunbar and the water vibrio. S. B. S.

Production of Citric Acid from Glycerol by Fungi. CARL WEHMER (*Chem. Zeit.*, 1913, **37**, 38—39. Compare A., 1893, ii, 591; 1909, ii, 602; 1910, ii, 60, 61).—When two species of *Citromyces* were grown in nutrient solution containing ammonium nitrate, potassium phosphate, magnesium sulphate, calcium carbonate, and glycerol (3—20%), large quantities of citric acid were produced. In the absence of calcium carbonate no such accumulation occurs, and it is assumed that, in the absence of any neutralisable base, any citric acid formed is destroyed immediately by the fungi. Similar growth takes place when the glycerol is replaced by sucrose, lactose, mannitol, xylose or arabinose. Sucrose is inverted, and reducing substances are formed in cultures supplied with glycerol. The author discusses the mechanism of citric acid formation from glycerol, and contests the view advanced by Mazé, that acid is only produced when there is a deficiency of nitrogen, or that it is in any way due to a lack of iron or zinc. H. B. H.

Action of Hydrogen Ions, Boric Acid, Copper, Manganese, Zinc, and Rubidium on the Metabolism of Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 753—764).—In investigating the culture conditions of *Aspergillus niger* it is not sufficient to merely ascertain the dry weight produced, as was done by Raulin and others. Spore formation, for instance, produces differences in composition. It is, therefore, desirable to determine the changes of the plastic equivalent, or of the assimilation quotient, several times during development.

Addition of 2·35 c.c. of *N*-sulphuric acid to 100 c.c. of culture solution and of 0·5% of boric acid has very slight effect on the plastic equivalent of the carbon.

A high weight of mycelium is not always a favourable indication. It was found that certain concentrations of copper sulphate, zinc chloride and sulphate considerably increase the plastic equivalent of the carbon, whilst the increase in the weight of mould is proportional to the retarded spore production. Very dilute zinc solutions have no effect; copper salts, in all dilutions, counteract spore formation. Minimal quantities of manganese do not alter the plastic equivalent of the carbon, but only affect the rate of metabolism. The amounts of dry matter found by Bertrand should be considered as values indicating the velocity of the process.

When potassium is replaced by rubidium, spore formation is checked, the weight of mould increased, whilst the metabolism of the carbon remains the same. N. H. J. M.

Influence of Zinc, Magnesium, Calcium, Potassium, and Sodium Salts on the Growth of Aspergillus niger. J. Buromski (*Centr. Bakt. Par.*, 1912, ii, **36**, 54—66. Compare A., 1908, ii, 124; 1911, ii, 222, 421, 664; 1912, ii, 377, 861).—The fungus was grown in a medium consisting of ammonium sulphate or nitrate 1%, sucrose 5%, magnesium sulphate 0·25%, monopotassium phosphate 0·5%, traces of ferrous sulphate, and distilled water. The addition of zinc sulphate in the proportion of 0·001—0·1% led to an increase in the respiratory coefficient (carbon dioxide crop): that of the control and treated cultures respectively being 1·8 and 2·4 at 30°, and 2·8 and 3·5 at 20°. The addition of calcium sulphate to magnesium-free medium decreased the growth of the organism; 0·25% magnesium sulphate to magnesium-free medium increased the crop very greatly, whilst calcium and magnesium sulphates increased the growth still more. The presence of calcium salts prevents the accumulation of oxalates in the cultures. Magnesium sulphate may be beneficially increased to 0·5%, although fructification begins to be affected at this concentration. Sodium salts proved to be without value, but increasing amounts of potassium salts caused corresponding increases of growth. Magnesium and potassium salts therefore, not only serve as nutrients, but also exercise a stimulative action. H. B. H.

Enzymatic Nature of Uric Acid and Hippuric Acid Fermentation. Alexander Kossowicz (*Chem. Zentr.*, 1912, ii, 1300, 1482; from *Zeitsch. Gährungsphysiol*, 1, 121—123, 317—319. Compare this vol., i, 146).—Filtered solutions from cultures of *Aspergillus niger*, *Mucor Boidin*, *Phytophthora infestans*, *Isaria farinosa*, and *Botrytis bassiana*, in which urea was present as only source of nitrogen, liberated ammonia from uric and hippuric acid, and from the latter, benzoic acid as well. A filtrate from *Cladosporium herbarum* only showed distinct production of ammonia in the case of uric acid. Similar results were obtained by means of the alcohol precipitates obtained from the filtrates from *Aspergillus* and *Cladosporium*.

Referring to Shibata's negative results with *Aspergillus niger* and uric acid, it was found in similar experiments that *Aspergillus niger*, *Mucor Boidin*, *Phytophthora infestans*, *Isaria farinosa*, *Botrytis bassiana*, and *Cladosporium herbarum* all produce ammonia from uric acid, and that all, except *Cladosporium*, decompose hippuric acid with production of ammonia and benzoic acid. N. H. J. M.

The Rate of Fermentation as Measured by Difference of Potential. M. C. Potter (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 230—231. Compare *ibid.*, 1910, 3).—It has been shown previously that during the fermentation of sugar by yeast an *E.M.F.* is developed. The author now finds that the measurement of the rate of fermentation by the development of the *E.M.F.* and by the evolution of carbon dioxide as in Slator's method are in close agreement, so that the electrical method provides a ready means of determining the rate of fermentation.

Experiments are also quoted, showing that the carbon dioxide given off during fermentation carries an electric charge, and that the rate of fermentation is uninfluenced by the potential of the fermenting liquid.
F. B.

Fermentations with Yeast in the Absence of Sugar. IX. Fermentation of Keto-acids by Wine Yeasts. CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, 47, 405—412).—Wine yeasts, of which a large number of German varieties were investigated, exert the same action on pyruvic acid as the beer yeasts, giving rise to acetaldehyde (which was isolated as its *p*-nitrophenylhydrazone) and carbon dioxide. These yeasts also attack oxalacetic acid and α-keto-*n*-butyric acid.
S. B. S.

Fermentations with Yeast in the Absence of Sugar. X. The Fermentation of α-Ketobutyric Acid CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, 47, 413—420).—This acid is very readily attacked by various yeasts and yeast preparations. The actual course of fermentation is not yet ascertained, in that propaldehyde could only be isolated in small quantity (about 4%). α-Ketoglutaric acid is also very readily attacked; phenylpyruvic acid is also fermented, but not αγ-diketovaleric acid.
S. B. S.

The Acidification of Musts by Yeasts during Alcoholic Fermentation. AUGUSTE FERNBACH (*Compt. rend.*, 1913, 156, 77—79). A study of the influence of the original acidity of the medium on the production of acids during the fermentation by yeasts of a saccharine liquid. Even in varying conditions the results show that the acidification produced by the yeasts, independently of their individual character, is subject to the acidity of the medium in which they function, low acidity in the medium favouring high acid production.
W. G.

Fixation of Elementary Nitrogen by Yeasts, Monilia candida, and Oidium lactis. ALEXANDER KOSSOWICZ (*Bied. Zentr.*, 1913, 42, 68—69; from *Zeitsch. Gährungsphysiol*, 1).—The results of experiments with (1) *Saccharomyces Pastorianus III Hausen*; (2) *Monilia candida*; (3) *Saccharomyces membranaefaciens*; (4) *Saccharomyces anomalus*; (5) *Oidium lactis*, cultivated in solutions containing sucrose (5%), glucose (0·2%), and mannitol (0·2%), in addition to minerals, showed in three months the following gains of nitrogen: (1) 4·8 and 5·2; (2) 6·2 and 6·8; (3) 6·9; (4) 7·4, and (5) 4·8 and 5·8 mg.

The air in the flasks was freed from combined nitrogen.
N. H. J. M.

Mode of Action of Dilute Solutions of Electrolytes on Germination. HENRI MICHEELS (*Bull. Acad. roy. Belg.*, 1912, 753—765. Compare A., 1910, ii, 883).—Germination experiments with wheat in electrolysed and non-electrolysed *N*/100-potassium chloride solutions through which chlorine was passed showed that chlorine was rendered more favourable by the cathode liquid and was poisonous in the non-electrolysed solution.

In the case of potassium hydroxide (25 c.c. of a 0·1% solution added to 500 c.c. of $N/100$-potassium chloride), a very injurious effect was observed in the non-electrolysed solution; its toxicity was diminished in the anodic liquid, but only in a slight degree.

Copper sulphate ($N/200$) in anodic solution, which is acid, is more toxic than the cathodic solution, which is only slightly acid. The solution is toxic when not electrolysed.

Comparing $N/100$-potassium chloride with electrolysed solutions in which the cathodic and anodic liquids received hydrochloric acid and potassium hydroxide respectively, the best results were obtained in the non-electrolysed solution and in the cathodic liquid notwithstanding the acidity, whilst the disappearance of the acidity of the anodic liquid only slightly diminished its toxicity.

The conclusion is drawn that anodic and cathodic liquids owe their characters in part to the liberated cations and anions, not passed to the chemical state. In solutions of electrolytes, the action of cations would not be exclusive, but only preponderating. N. H. J. M.

Effects of Manurial Salts on the Germination of Different Plants. ALBERT RUSCHE (*J. Landw.*, 1912, **60**, 305—365; from *Diss.*, Göttingen, 1912).—Potassium chloride does not act unfavourably on the germination of cereals, peas, rape, and beet, but is unfavourable in the case of clovers, serradella, lucerne, and lupins, especially white clover and serradella. Sodium chloride is more unfavourable than potassium chloride, except with barley, lupins, serradella, and rape. Magnesium and calcium chlorides generally have the same effect as potassium chloride, but not in every case; whilst ammonium chloride is injurious, especially with clovers. Nitrates are generally more favourable than chlorides; ammonium nitrate, however, resembles the chloride. Potassium sulphate is generally favourable, except with serradella; sodium sulphate is similar in its effects, whilst magnesium and calcium sulphates are also favourable. Of all the salts employed, sodium and potassium carbonates are the most favourable.

As regards the length of roots, nitrates produced the shortest roots with cereals. The longest roots were obtained with sulphates and phosphates.

In the case of peas the longest roots were obtained when no manure was employed. With red clover the longest roots were produced under the influence of sulphates and carbonates, the shortest with carbonates and chlorides.

The full results relating to germination, length and weight of roots, and the development of the above-ground parts of the different plants are given in numerous tables. N. H. J. M.

Influence of Previous Conditions on the Value of the Respiratory Quotient of Green Leaves. LÉON MAQUENNE and EM. DEMOUSSY (*Compt. rend.*, 1912, **156**, 28—34).—The authors have studied a number of abnormal cases where the respiratory quotient of leaves gathered in full sunlight was considerably lower than that of leaves which had been kept in the dark for several hours. They worked with leaves of sorrel, stonecrop, geranium, rhubarb, and *Sedum*

acre, and from their results they consider that the respiration of a plant is effected in two successive phases; the first leading to a production of fixed acids, the result of an oxidation rendered incomplete owing to the slowness of penetration of the oxygen; the second to a combustion of these acids. It is necessary also to take into account the solution of the carbon dioxide in the cell-sap and the temperature, which has an influence both on the acidification and the absorption of carbon dioxide by the leaf.

Working with an *Aspidistra* leaf and observing the variation of pressure, using their manometric measuring apparatus (compare A., 1912, ii, 1201), they find that with leaves taken straight from the sunlight the pressure at first diminishes and then rises, whilst with leaves kept in the dark for some hours before measuring, the pressure rises immediately and continuously. W. G.

Hydrolysis and Displacement by Water by Nitrogenous and Mineral Substances Contained in Leaves. GUSTAVE ANDRÉ (*Compt. rend.*, 1912, **155**, 1528—1531. Compare A., 1912, ii, 198).—Chestnut leaves show much the same loss of nitrogen, phosphoric acid, and potassium, by exosmosis, when steeped in water, as do grains of wheat and haricot beans (compare A., 1912, ii, 591). After 255 days steeping, the leaves had lost 6·27% of their nitrogen, 74·14% of phosphoric acid, and 94·58% of potassium. Most of the loss occurred in the first few days, and it was found to be more rapid the younger were the leaves. W. G.

Does Potassium Participate in the Building Up and Degradation of Carbohydrates in Higher Plants? JULIUS STOKLASA and E. SENFT (*Zeitsch. landw. vers. Oesterr.*, 1912, **15**, 711—736).—It is found that by the action of ultraviolet rays on nascent carbon dioxide and hydrogen in the presence of potassium hydroxide a photosynthesis occurs with the formation of formaldehyde, and that the latter subsequently condenses to furnish sugars; the reduction of carbon dioxide in the cell does not take place in the absence of potassium hydrogen carbonate, even in the presence of nascent hydrogen; and formic acid (which is subsequently reduced) is also found to be one of the products of this reaction. F. M. G. M.

Enzyme Synthesis. III. Diastase and Starch of Plant Tissues. HAROLD C. BRADLEY and E. KELLERSBERGER (*J. Biol. Chem.*, 1913, **13**, 425—430).—With some exceptions the results in this series are more favourable to the view of enzyme synthesis in the tissues, for no tissues which contain starch are destitute of diastase, although many tissues which contain diastase are free from starch. W. D. H.

Occurrence of Arsenic in the Vegetable Kingdom. F. JADIN and A. ASTRUC (*J. Pharm. Chim.*, 1912, [vii], **6**, 529—535).—The occurrence of arsenic in the vegetable kingdom appears to be general, as the authors have detected its presence in some sixty-seven different kinds of vegetables, fruits, cereals, plants, parasitic plants, fungi, etc.

The quantity of arsenic found per 100 grams of substance varied from 0·008 mg. in dates to 0·266 mg. in radishes. Parasitic plants contained arsenic, even although they were not in direct contact with the soil, but there was no relation between the amounts of arsenic in the parasite and its support. Plants belonging to the same family do not invariably contain similar quantities of arsenic, but in the case of one and the same plant the portions containing chlorophyll contained more arsenic than the parts not exposed to light. It is pointed out that one of the sources of the arsenic found in animal organs lies in the vegetable substances consumed as food. W. P. S.

Stimulative Action of Manganese and Copper Sulphates on Plants. L. Montemartini (*Bied. Zentr.*, 1913, **42**, 65; from *Staz. sper. agrar. ital.*, 1911, **41**, 564).—Manganese and copper sulphates absorbed from aqueous solutions stimulate respiration, the effect varying with different plants. Vine plants are stimulated by 0·001% manganese sulphate, whilst greater concentrations are injurious, and are injured by 0·01% of copper sulphate. Garden beans, and still more potatoes leaves, are more resistant and more stimulated.
N. H. J. M.

Demonstration of Carotinoids in Plants. Separation in Crystalline Form. C. van Wisselingh (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 511—526).—The various methods employed in detecting the presence of carotinoids are described. Indications were obtained that several distinct carotinoids frequently occur in plants.
N. H. J. M.

Demonstration of Carotinoids in Plants. Behaviour of Carotinoids towards Reagents and Solvents. C. van Wisselingh (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 686—692).—In presence of carotinoids a blue coloration is produced by strong sulphuric, sulphurous, and nitric acids, bromine water, and strong hydrochloric acid with a little phenol or thymol; iodine dissolved in potassium iodide solution or chloral hydrate gives a green coloration. Two new reagents were also employed: concentrated solutions of antimony trichloride and of zinc chloride, both in 25% hydrochloric acid, which colour crystals of caratinoids dark blue.

Lists of flowers and other parts of plants which were tested with the different reagents are given. N. H. J. M.

Demonstration of Carotinoids in Plants. Leaf of Urtica dioica, the Flower of Dendrobium thyrsiflorum and Hæmatococcus pluvialis. C. von Wisselingh (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 693—700).—The flower of *Dendrobium thyrsiflorum* contains two carotinoids, one of which, of a reddish-orange colour, is not common in plants, and perhaps belongs to the xanthophylls. The examination of *Haematococcus pluvialis* indicated the presence of a greater number of carotinoids than have hitherto been detected (compare Zopf, *Biol. Centr.*, 1895, **15**, 417; H. C. Jacobson, *Folia Microbiol*, 1912, **1**, 24). N. H. J. M.

Mannitol in the Sap of Asparagus. E. Busolt (*J. Landw.*, 1912, **60**, 393—396).—The mannitol in the sap of asparagus is produced by fermentation, and is not originally present.

N. H. J. M.

Presence of Stachyose in the Haricot and in the Seeds of Some Other Leguminoseæ. Georges Tanret (*Compt. rend.*, 1912, **155**, 1526—1528).—The author has isolated stachyose in a crystalline form, by means of its strontium compound, from the haricot bean and the seeds of certain other leguminoseæ, namely, lentils, clover, galega, lupin, and the soja bean. In all cases sucrose was present as well. The lupeose, obtained as an uncrystallisable syrup from haricots and lupins by Schulze, was, therefore, stachyose in an impure state. No stachyose could be isolated from pea-seeds.

W. G.

Presence of Adenine and Aspartic Acid in Mulberry Leaves. Z. Mimuroto (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, **5**, 63—65).—From 500 grams of air-dried mulberry leaves, 1·2 gram of adenine (as picrate) and 0·3 gram of aspartic acid were obtained.

N. H. J. M.

Action of Stimulants on Rice. Manuel Rocas (*Bied. Zentr.*, 1913, **42**, 41—42; from *Philippine Agric. Forester*, 1912, 1, 89).—Previous investigations indicate that there are no poisons which cannot act as stimulants on plants; that compounds of gold, silver, platinum, mercury, tungsten, palladium, copper, nickel, cobalt, boron, tin, cadmium, tellurium, arsenic, iodine and fluorine are poisonous, whilst chromium, manganese, bismuth, sulphur and magnesium are only poisonous under certain conditions.

The following concentrations of the various compounds were found to be favourable: sodium borate, 1/1000; manganese sulphate, 1/1000; ferrous sulphate, 1/1000; ferric chloride, 1/5000; copper sulphate, 1/2000; nickel sulphate, 1/5000; cobalt nitrate, 1/10,000, and zinc sulphate, 1/1000 mol. solutions.

Mercuric chloride in 1/50,000 mol. solutions inhibited growth, whilst ferric chloride and copper sulphate (1/1000) are injurious, and sodium borate (1/100) somewhat injurious.

The optimum results for rice are generally much higher than previous experiments have shown for other plants. The experiments were, however, not made with water-cultures, but in soil. N. H. J. M.

Presence of Nicotinic Acid in Rice Bran. Umetaro Suzuki and S. Matsunaga (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, **5**, 59—61).—Nicotinic acid was obtained from rice bran, freed from fat, by extracting with 80—85% alcohol. The acid had not previously been found in any vegetable substance. The yield of picrate amounted to about 1 gram from 1 kilo. of bran. N. H. J. M.

The Substitution of Different Chemical Elements for Zinc in the Culture of Sterigmatocystis nigra. Maurice Javillier (*Compt. rend.*, 1912, **155**, 1551—1552).—The author has

replaced the zinc in the culture medium of *Sterigmatocystis nigra* by a wide range of other elements, and, with the exception of one, namely, cadmium, they were all without influence on the crop. While the addition of zinc to the extent of 1 in 10,000,000 produces a crop 6·2 times as great as in its absence, the same concentration of cadmium produces a crop only 2·6 times as great, and cadmium has a marked injurious effect on the sporulation. W. G.

Volatile Aliphatic Acids of Corn Silage. Arthur W. Dox and Ray E. Neidig (*J. Amer. Chem. Soc.*, 1913, **35**, 90—93).—With reference to the work of Hart and Willaman (Abstr., 1912, ii, 1205) on the volatile fatty acids and alcohols in maize silage, the authors draw attention to their own paper on the subject (*Iowa Agric. Exp. Sta., Research Bull.*, 1912, 7, 32). The results are in fair agreement, except with regard to formic acid and methyl alcohol; in the latter investigation, only traces of formic acid were found and methyl alcohol was absent, whereas Hart and Willaman found 17% of formic acid in the volatile acids and 21% of methyl alcohol in the alcohols. Certain sources of error are pointed out in the methods employed by Hart and Willaman, and it is considered that these may account for the discrepancies. E. G.

Action of Long-continued Exclusive Manuring on Plants and Soils. S. Graf Rostworowski (*J. Landw.*, 1912, **60**, 371—392). —The results of experiments with potatoes showed that, when there is a tendency to leaf curl, it is desirable to employ potassium salts in moderation.

As regards the effect of manures on the composition of potato ash it was found that the ashes of potatoes from plots manured with potassium and with potassium + phosphorus + nitrogen were almost identical in composition, and there was also no difference between the ashes of potatoes from plots manured with nitrogen and the unmanured plot.

The composition of the ash of potato leaves varied considerably with different manures; potash varied from 5% (unmanured) to 33% (potassium manure), and lime varied from 21% (potassium alone, or with phosphorus and nitrogen) to 41% (unmanured). Application of sodium nitrate resulted in a high percentage of sodium in the leaf ash.

Notwithstanding the long-continued application of potassium manures, the potash in the ash of the tubers never reached 60%.

Experiments were also made to ascertain the effect of the long-continued manuring on the soil. N. H. J. M.

Chemical and Physical Nature of "Roterden." Edwin Blanck (*J. Landw.*, 1912, **60**, 397—400).—A reply to Hissink (A., 1912, ii, 981; compare van der Leeden and Schneider, *Internat. Mitt. Bodenkunde*, 1912, 2, 81). N. H. J. M.

Analysis of a Florida Clay. Archibald A. Hall (*Proc. Univ. Durham Phil. Soc.*, 1912, **4**, 228—229).—The author gives an analysis of a clay subsoil underlying peat, from Duval in the great swamp of Florida, and points out that the composition of this clay, on which

vegetation is now growing under conditions which approximate to those of the coal age, is very similar to that of a typical underclay, underlying coal. F. B.

Osmosis in Soils. Soils Act as Semipermeable Membranes. I. C. J. LYNDE (*J. Physical Chem.*, 1912, **16**, 759—765).—The movements of water in soil have been attributed to gravitation, capillary action, and heat. To these must now be added osmotic pressure.

Osmotic cells of the Pfeffer type were prepared as follows: Glass tubes 150 mm. × 11 mm. diameter were closed at one end with cotton cloth and wire gauze. A layer of sterilised heavy clay subsoil was deposited in each tube, and consolidated against the cloth by centrifugal action. The tubes were filled up with 10% sugar solution, or 10% potassium sulphate solution, and immersed in distilled water. In each case water diffused into the cells osmotically through the clay. The rate of diffusion inwards was considerably greater at 24·5° than at 22·5°. It is probable that the solution leak outwards through the clay was considerable. R. J. C.

Osmosis in Soils. Soils Act as Semipermeable Membranes. II. C. J. LYNDE and F. W. BATES (*J. Physical Chem.*, 1912, **16**, 766—781. Compare preceding abstract).—Three pairs of osmotic cells were prepared with clay subsoil as already described, the layers of sterilised clay being 54 mm., 36 mm., and 18 mm. thick respectively. The solution filling the cell was the aqueous extract of the clay forming the membrane in each case. The cells were closed by rubber stoppers carrying capillary tubes. The predetermined capillary rise of each solution was deducted from the total rise, the remainder being the osmotic rise.

The osmotic pressures obtained with the thickest layers of clay were the highest, but the concentrations of the soil solutions were also highest in these cases. On the assumption that the osmotic pressures should be equal to these given by solutions of potassium chloride of equal electrical conductivity, the osmotic efficiency of the membranes was calculated to be only 2·5% (54 mm. membrane), 1·4% (36 mm.), and 1·0% (18 mm.), the efficiency being roughly proportional to the thickness of the membrane. An experiment with a membrane of clay 108 mm. thick gave still higher pressures. It is calculated that about 2 metres thickness of clay would be a perfect semipermeable membrane. In all cases the osmotic rise at 36·5° was somewhat higher than at 16·7°.

The soil used in the above experiments had the physical composition: sand 10·5%, silt 50·4%, clay 36·3%, organic matter 2·8%. A number of soils containing 44—61% of sand and only 12—16% of clay failed to show any decided osmotic properties.

It is suggested that osmotic effects play an important part in agricultural operations, particularly on heavy clay subsoils. Tillage, drainage, manuring, and mulching by favouring bacterial action increase the proportion of soluble matter in the soil, and therefore the amount of moisture which is raised osmotically through the subsoil. The same

effect may be brought about by the addition of mineral fertilisers and such substances as gypsum and salt which are not directly plant foods. There may be other substances which are not plant foods, but might be beneficial as fertilisers from the osmotic point of view. R. J. C.

Importance of the Error of Analysis in Questions Relating to the Nitrogen Economy of Arable Soils. THEODOR PFEIFFER and EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1912, **78**, 367—374).—A final attempt was made to obtain a satisfactory nitrogen balance with the experimental soils at Breslau. Six plots (9 sq. metres each) were selected, which had given similar amounts of crops during two years, and from each plot five samples of soil were taken. Ten or twelve nitrogen estimations were made with each sample. The experimental error was found to be ±0·00086, which would correspond with 25·8 kilos. of nitrogen per hectare to a depth of 25 cm. if the weight of the soil is taken as 3,000,000 kilos., or 32·2 kilos. if the total weight of soil is taken as 3,750,000 kilos. As this number has to be multiplied by three it would only be possible to show a difference exceeding 77·4 or 96·6 kilos. of nitrogen per hectare. With fewer samples or analyses the error would, of course, be greater. It must also be borne in mind that the nitrogen of crops is not all derived from the surface soil, but from the subsoil as well. N. H. J. M.

Estimation of the Value of Plant Foods in Soils and Manures so far as Dependent on Solubility. J. G. MASCHHAUPT and L. R. SINNIGE (*Bied. Zentr.*, 1913, **42**, 16—20; from *Verslag. Landbouwkund. onderzoek. Rijkslandbouwproefstat.*, 1912, No. 11).—Single extractions of different phosphates with a definite volume of water containing carbon dioxide will not show the relative values of the manures. Better results will be obtained when successive extracts are made, and it is probable that a method of continuous extraction in which the dissolved substances are at once removed will give better results than intermittent extraction.

Repeated extraction with fresh amounts of citric acid solution will probably indicate the relative values of phosphates. As, however, carbon dioxide is the chief solvent at the disposal of soil and roots, it is to be preferred to citric acid. N. H. J. M.

Antagonism between Anions as Affecting Ammonification in Soils. CHARLES B. LIPMAN (*Centr. Bakt. Par.*, 1913, ii, **36**, 382—394).—Experiments in soils on the lowering of the toxicity of salts by the addition of other salts, as measured by the amount of ammonia produced. The first series, which deals with the antagonism between the salts of "white alkali," sodium chloride and sulphate, showed that addition of sodium chloride (0·2%) to the soil reduced the amount of ammonia from 54·46 to 30·73 mg., whilst the further addition of sodium sulphate (0·3%) increased the amount to 37·1 mg., less effect being produced by smaller or larger amounts of sulphate. In an experiment with sodium chloride and carbonate, the ammonia was reduced from 41·75 to 22·05 mg. by 0·2% of sodium chloride; sodium carbonate in amounts of 0·2% and more increased the ammonia

production, the greatest amount being 70·7 mg. with 0·7% of sodium carbonate in addition to 0·2% of chloride.

Further experiments are described in which sodium sulphate and carbonate were employed.

The results show that antagonism is shown most strongly between sodium carbonate and sodium chloride; next between sodium carbonate and sodium sulphate, and least between sodium chloride and sodium sulphate.

When 0·3 or 0·4% of sodium carbonate is added to soil containing 0·9% of sodium sulphate there is an increased toxic effect; when, however, the amount of carbonate is increased to 0·5%, the toxic effect of the sulphate is reduced, and with 0·6% of carbonate it is still further reduced. N. H. J. M.

Influence of Organic Substances on the Decomposition and [Manurial] Action of Nitrogenous Compounds. Max Gerlach and Alfred Densch (*Bied. Zentr.*, 1913, **42**, 21—30; from *Mitt. Inst. Landw. Bromberg*, 1912, **4**, 259).—Pot experiments in which slightly humus, loamy sand manured with sodium nitrate both alone and with dextrose and straw respectively; with an ammonium salt, alone and with dextrose; and with dextrose and straw respectively, was kept for two months, after which the amounts of total nitrogen and the nitrates and soluble organic nitrogen were estimated. The results showed that the total nitrogen changed very little, and indicated that the nitrogen added as ammonium salt and as nitrate was converted into insoluble proteins.

The same soil was then utilised for a series of vegetation experiments from April, 1909, to August, 1911, during which time, oats, mustard, rye, mustard and wheat were grown.

Dextrose and straw was always unfavourable to oats, but were beneficial to next plants (mustard). The final results relating to nitrogen did not show any greater increase when dextrose was added than without. Nitrogen applied as nitrate showed no loss, whilst application as ammonium sulphate resulted both in loss and gain. Straw alone and in conjunction with nitrate had only a slight effect on the total nitrogen.

The results indicate that ammonium salts and nitrates are converted into insoluble proteins in presence of undecomposed organic substances, and that the insoluble nitrogen compounds readily decompose into substances which plants can utilise. N. H. J. M.

Relation of Active Potash to Pot Experiments. George S. Fraps (*J. Ind. Eng. Chem.*, 1912, **4**, 525—526).—An account of pot experiments with representative Texas soils, from which the conclusions are drawn that (1) the percentage of crops deficient in potash decrease with the increase of active potash in the soil; (2) the percentage of crops injured by potash increase with the active potash in the soil; (3) the effect of fertiliser potash on the weight of the crop decreases as the active potash content of the soil increases; (4) the percentage of potash in the crop increases as the active potash in the soil increases; (5) the total potash removed by the crop from

the soil increases as the active potash content of the soil increases. The term "active potash" is applied to that which is soluble in $N/5$-nitric acid. F. M. G. M.

Effect of Sugar on the Fertility of Soils. Theodor Pfeiffer and Edwin Blanck (*Landw. Versuchs-Stat.*, 1912, **78**, 375—388).—The results of plot experiments in which oats, beet, and oats were grown successively both without and with sugar and phosphoric acid, and with both sugar and phosphoric acid, showed that the application of sugar was slightly injurious the first year, and resulted in a slight increase the second year. In the third year there was no appreciable difference due to sugar. No evidence of increased fixation of nitrogen was obtained. N. H. J. M.

Calcium Cyanamide. C. J. Milo (*Chem. Zentr.*, 1912, ii, 1054—1055; from *Med. Proefstat. Java-Suikerind.*, 1912, 427—527). —When calcium cyanamide is used as a manure, the lime is readily taken up and held by the soil, but the nitrogen is not held so well as in the case of ammonium sulphate. In spite of this no nitrogen is lost if the cyanamide is applied in the dry season and the soil is not heavily watered immediately afterwards, and none is lost by volatilisation if the manure is properly applied. The nitrogen is utilised mainly by bacterial agency, but is also absorbed in other ways. Comparison of calcium cyanamide with ammonium sulphate as a manure has not yet given definite results. Dicyanodiamide is not poisonous to sugar-cane, and although calcium cyanamide shows some toxic effects, it appears to be rapidly converted into harmless cyanamide in the soil.

T. A. H.

Behaviour of Calcium Cyanamide when Stored, and under the Influence of Soil and Colloids. G. Henschel (*Bied. Zentr.*, 1913, **42**, 33—34; from *Cent. Bakt. Par.*, 1912, ii, **34**, 279).—Dry sterilised soil or colloids decompose cyanamide more quickly than when not sterilised. Under sterilised conditions, urea and dicyanodiamide are formed, but no ammonia. Experiments with different soils showed almost complete agreement between the intensity of the decomposition when sterilised and the production of ammonia when not sterilised; an exception, however, occurred in the case of a sandy soil containing much humus, which showed a strong colloid, but feeble bacterial, action.

When cyanamide is stored, a good deal of urea may be produced under some conditions; different preparations show, however, considerable differences, both in this and other respects. No loss of nitrogen was ever observed, the lower percentages of nitrogen after storing being due to absorption of water and carbon dioxide. N. H. J. M.

Organic Chemistry.

Some Reactions of Sodamide in the Presence of Liquid Ammonia. Formation of Ethylene Hydrocarbons. E. CHABLAY (*Compt. rend.*, 1913, **156**, 327—330).—By the addition of alkyl iodides or chlorides to sodamide in liquid ammonia, primary amines are not the only products as has been supposed (compare Lebeau, A., 1905, i, 401, 512), but at the same time, except in the case of the methyl haloids, the corresponding olefine is formed in varying amounts. Starting from the ethyl haloids, the yield of olefine increases on passing up the series, and is always greater when using the chlorides than if the iodides are employed; thus *iso*butyl iodide gives a yield of 62·4% of *iso*butylene, whilst the chloride gives a yield of 83·6%. In this reaction sodamide resembles alcoholic potassium hydroxide in its behaviour (compare Meunier and Desparmet, A., 1907, i, 186).

W. G.

The Adsorption of Acetylene by Palladium Black. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1913, **46**, 128—132).—In the previous investigation on the same subject (A., 1910, i, 807), the palladium black was suspended in aqueous solutions of various substances. The authors have now investigated the adsorption of acetylene, using either suspensions of palladium black in pure water, or else dry palladium black. The experiments in which 60% alcohol was used in place of pure water were also repeated.

In all cases the adsorption of the acetylene takes places slowly, and the results given do not point to any fixed ratio between the weight of palladium and the amount of gas adsorbed. It is probable that the acetylene is not completely adsorbed as such, but undergoes partial polymerisation.

When the dry palladium black is not completely free from oxygen, formation of feeble sparks occurs immediately it is brought into contact with the acetylene.

T. S. P.

Acetylene or Acetylidene Compounds. The "Oxidation Rearrangement." HEINRICH BILTZ (*Ber.*, 1913, **46**, 143—149).—Nef and his school assign to the halogen substitution products of acetylene an acetylidene formula, as, for example, $CI_2\colon C$, di-iodoacetylidene. No definite proof of this constitution has been afforded, and the facts observed are more in favour of the acetylene structure, $CI\vdots CI$. Di-iodoacetylene is very readily formed from acetylene by the action of hypoiodites and iodine, the process involving simple substitution of iodine for hydrogen.

The reasons for the representation of dibromoacetylene as $CBr\vdots CBr$ are discussed.

E. F. A.

Sodium Silver Thiosulphate and Acetylene-Silver Acetylide. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1913, **79**, 355—356).—Sodium thiosulphate is added to an ammoniacal solution

of silver nitrate, and acetylene is passed through the clear solution. The yellow precipitate is collected, washed with water and alcohol, and dried in air. It is stable in dry air, but is decomposed by water, yielding a brick-red product. The final products of decomposition are silver sulphide and sodium sulphate.

The yellow compound is soluble in ammonia, and is re-precipitated by acids, again dissolving in an excess to form unstable solutions, which evolve sulphur dioxide and acetylene. Analysis leads to the formulæ $2Na_2S_2O_3,7Ag_2S_2O_3,18Ag_2C_2,32C_2H_2$ for the yellow compound, and $4Ag_2S_2O_3,7Na_2S_2O_3,86Ag_2C_2,13C_2H_2$ for the red compound.

C. H. D.

The Production of Chlorine Substitution Products of Methane from Natural Gas. CHARLES BASKERVILLE and H. S. RIEDERER (*J. Ind. Eng. Chem.*, 1913, **5**, 5—8).—The authors have investigated the conditions necessary for the chlorination of the methane present in natural gas, especially those which would lead to the formation of carbon tetrachloride, from which chloroform could be obtained by reduction. The apparatus used was so designed that the gases could be constantly circulated through it, the circuit always containing a heater for heating the gases, and a condenser for condensing out the products formed. In the first trials the circuit also contained an arc, either between carbon or iron terminals, but this was omitted later, as it was found that chlorination was not effected by the combustion taking place in the arc. It was ultimately found that the primarily important condition for the chlorination is a source of light rich in the rays of the visible blue spectrum, that is, the spectrum from the bluish-green through the visible violet. The ultraviolet part of the spectrum plays little part in the reaction. Apparently the necessary source of light may be obtained by an arc, between iron electrodes, in the circuit, and in some experiments a 20—25% yield of a mixture of carbon tetrachloride and chloroform was obtained.

T. S. P.

Primary Dinitro-, Nitro-nitrite and Dialdoxime Compounds of the Aliphatic Series. II. Derivatives of the Heptane Series and Synthesis of Pimelaldehyde. JULIUS VON BRAUN and E. DANZIGER (*Ber.*, 1913, **46**, 103—110).—As has already been shown (von Braun and Sobecki, A., 1911, i, 830), the action of silver nitrite on aliphatic compounds of the type $I\cdot[CH_2]_n\cdot I$ gives a mixture of dinitro, nitro-nitrite, and dinitrite derivatives, the first two of these being reducible to dialdoximes and amino-alcohols respectively. These changes have already been performed with n equal to 4, 5 and 10, and are now extended to the heptamethylene chain.

$\alpha\eta$-Di-iodoheptane was prepared from $\alpha\epsilon$-dibromopentane by conversion of the latter into an organo-magnesium compound, causing this to react with monochloromethyl ether (compare Dionneau, A., 1906, i, 134) and hydrolysing the product with hydriodic acid. It was also obtained by the stages: dibromopentane, diaminopentane, dichloroheptane, and diphenoxyheptane, the last of which again is converted into di-iodoheptane by hydriodic acid. In the conversion of dichloro-

heptane into diphenoxyheptane by sodium ethoxide, a small quantity of α-phenoxy-ζ-methylene-n-hexane, b. p. 145°/12 mm., was obtained as by-product.

αη-Di-iodoheptane reacts vigorously with silver nitrite, producing a mixture which can be separated at 10 mm. into three fractions, b. p. 108—140° (mainly *heptamethylene nitrite*, $NO_2\cdot[CH_2]_7\cdot NO_2$), 140—160° (mainly *η-nitroheptyl nitrite*), and 160—205°, the last on refractionating yielding pale yellow *αη-dinitroheptane*, b. p. 198—200°/10 mm. The second fraction when reduced with tin and hydrochloric acid yields *η-hydroxyheptylamine*, a strong base, b. p. 150—152°/10 mm.; *benzoyl*, *nitrobenzoyl*, and *picrate* derivatives are oily; *platinichloride*, solid, m. p. 157°.

αη-Dinitroheptane when treated with sodium ethoxide in alcoholic solution gives an immediate precipitation of the white *sodium* salt, the aqueous solution of which can be used for the preparation of the salts of the heavier metals, for example, the *copper* (green), *barium* and *calcium* salts; with bromine, it forms an oily *bromide* (compare von Braun and Sobecki, *loc. cit.*), and with a diazobenzene solution there is obtained yellowish-red *αη-bisphenylazo-αη-dinitroheptane*,

$$N_2Ph\cdot CH(NO_2)\cdot[CH_2]_5\cdot CH(NO_2)\cdot N_2Ph,$$

m. p. 139°.

The reduction of a solution of the sodium salt of dinitroheptane by gradual addition to a solution of stannous chloride in hydrochloric acid gives *pimelaldoxime*, $OH\cdot N:CH\cdot[CH_2]_5\cdot CH:N\cdot OH$, a pale yellow, crystalline powder, m. p. 150—151°, from which, on boiling with dilute sulphuric acid, pimelaldehyde is not obtained, as it partly polymerises to a viscous oil, and partly becomes dehydrated to tetrahydrobenzaldehyde, semicarbazone, m. p. 211—212° (Wallach, A., 1906, i, 563). *Pimelaldehyde*, a pungent, colourless oil of b. p. 110—112°/13 mm., D_4^{20} 0·9895, is obtainable by the action of nitrous fumes on a suspension of the dioxime in cooled water until no more nitrous oxide is liberated; it readily reduces Fehling's solution, and an ammoniacal silver solution, and gives a *semicarbazone*, m. p. 183°; the *phenylhydrazone* and p-*nitrophenylhydrazone* are oily, whilst the *diphenylmethanedimethyldihydrazone*, $CH_2<\begin{matrix}C_6H_4\cdot NMe\cdot N:CH\\ C_6H_4\cdot NMe\cdot N:CH\end{matrix}>[CH_2]_5$ (structure not proved), is a yellow solid, m. p. 96—97°. The aldehyde resembles adipaldehyde in showing much less tendency to polymerise than do the other dialdehydes of this series.

A preliminary investigation has shown that glutaraldoxime when heated with mineral acids gives pyridine, probably by reason of the condensation of glutaraldehyde and hydroxylamine which are first formed. D. F. T.

Synthesis of an Unsaturated Hydrocarbon. CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, **10**, 60—63).—A note on the preparation of unsaturated alcohols by the interaction of unsaturated aldehydes and unsaturated haloids in presence of zinc and ether, and the conversion of such alcohols into unsaturated hydrocarbons by heating with potassium hydrogen sulphate. On treatment with zinc filings or shavings and ether, crotonaldehyde and allyl iodide give a

good yield of *αε-heptadiene-δ-ol*, $CHMe:CH\cdot CH(OH)\cdot CH_2\cdot CH:CH_2$. Its properties are still uninvestigated, but heating with potassium hydrogen sulphate converts it into a liquid. Repeated fractionation, finally over sodium, at 758 mm. gives three fractions, b. p. 105—110°, 110—112°, and 112°. On cooling to −76°, these three fractions solidify. The first has m. p. −35° to −32°, the second −23° to −21°, and the third −15° to −14·5°. One of these substances is believed to be an *αγε-heptatriene*, and their constitutions are to be determined. It is anticipated that the method will prove of general application.

A. J. W.

History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1913, **26**, 46—47).—Polemical against Schelenz (this vol., i, 2).

T. S. P.

Action of Magnesium on a Mixture of Ethyl *iso*Valerate and Allyl Bromide. G. MOSKALENKO (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1862—1865).—Decomposition by means of water of the product of the reaction of magnesium, ethyl *iso*valerate, and allyl bromide yields *diallylisobutylcarbinol*, $CHMe_2\cdot CH_2\cdot C(OH)(CH_2\cdot CH:CH_2)_2$, which forms a colourless, mobile liquid, b. p. 92°/37 mm., D_4^{23} 0·8616, n_D^{23} 1·45682, and exhibits the normal molecular weight in freezing benzene or boiling ether.

T. H. P.

Adipiopinacone. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1913, **27**, 25—26).—*Adipopinacone*, $OH\cdot CMe_2\cdot[CH_2]_4\cdot CMe_2\cdot OH$, m. p. 88—89°, is obtained in the form of its *hydrate*, containing $2H_2O$, by the action of magnesium methyl bromide on ethyl adipate. The hydrate is obtained in large, white crystals, m. p. 56·5°, which effloresce in air, and completely lose their water of hydration when left in a vacuum desiccator. By the action of warm dilute sulphuric acid, the pinacone is readily converted into *tetramethylhexamethylene oxide*, $O<\begin{matrix}CMe_2\cdot CH_2\cdot CH_2\\ CMe_2\cdot CH_2\cdot CH_2\end{matrix}$, a liquid with an ethereal odour, b. p. 156—157°/756 mm.

W. G.

Action of Magnesium on a Mixture of Allyl Bromide and Ethyl Levulinate. E. SCHTSCHERICA (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1853—1858).—The interaction of magnesium, allyl bromide (1 mol.), and ethyl lævulate (1 mol.), and subsequent decomposition of the product with water, should yield the ester,

$$C_3H_5\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

but this reaction could not be realised. No matter whether 1 mol. or 3 mols. of allyl bromide were employed, the resultant compound was always the *γ-glycol*, $C_3H_5\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot C(C_3H_5)_2\cdot OH$, which is a faintly yellow, syrupy, slightly mobile liquid with a characteristic odour, b. p. 157—159°/10 mm., D_4^{25} 0·9545, n_D^{25} 1·48712. When boiled with 20% sulphuric acid solution, the glycol is converted into the corresponding *oxide*, $\begin{matrix}CH_2\cdot CMe(C_3H_5)\\ CH_2\cdot C(C_3H_5)_2\end{matrix}>O$, which is an almost colour-

less liquid with a peculiar pleasant odour, b. p. 104·5–105·5°/10 mm., D_4^{25} 0·8905, n_D^{25} 1·46915, and has the normal molecular weight in boiling ether. T. H. P.

Synthesis of Lecithin. ADOLF GRÜN (*Ber.*, 1913, **46**, 125—127).—Polemical. A reply to Langheld (this vol., i, 155; compare Grün and Kade, this vol., i, 158). E. F. A.

Thionium Dibromides of Sulphides. VLADIMIR V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1902, **44**, 1885—1894).—The action of bromine on ethyl sulphide in carbon tetrachloride solution yields the thionium dibromide, SEt_2Br_2, which forms yellow crystals and resembles oxonium compounds in its general characters, and also as regards the nature of the solvents in which it dissolves readily or with difficulty. With acetic acid, it forms solid solutions, but in freezing benzene it exhibits the molecular weight, 199—211, the theoretical value being 250.

By excess of water, the dibromide is rapidly decolorised with development of a considerable quantity of heat and the formation of a white emulsion. Concentrated ammonia solution decomposes the thionium dibromide much less energetically than the corresponding oxonium compound, heat being developed and an oily layer of the sulphide formed at the surface of the liquid. Sodium hydrogen sulphite solution effects the decomposition rather more rapidly, and concentrated potassium hydroxide solution much more rapidly, than does water. Moist silver oxide converts these dibromides into the corresponding oxides, for example, $SMe_2\colon O$, which are appreciably more stable than the analogous oxonium compounds.

The heat of formation of the diethyl dibromide from the alkyl sulphide and bromine is 14·15 Cal. per gram-mol., that of the diamyl dibromide being 12·91 Cal. Measurement of the amounts of heat evolved when the reaction proceeds in carbon tetrachloride solutions of various concentrations shows that the solvent is virtually without influence in this respect.

As the heats of formation of the oxonium compounds corresponding with the above thionium compounds are 9·13 Cal. for $OEt_2\colon Br_2$ and 8·72 Cal. for $O(C_5H_{11})_2\colon Br_2$, it is to be expected that alkyl sulphides would displace the ethers from oxonium compounds. Calorimetric investigations show that when the oxonium compound is prepared in absence of solvent, such displacement does occur, but does not proceed to completion, at any rate within the limits of time available for calorimetric measurements; it appears probable that the bromine finally becomes distributed between the sulphide and the ether. When, however, a carbon tetrachloride solution of ethyl sulphide (1 mol.) is added to a solution of ether (1 mol.) and bromine (1 mol.) in the same solvent, 13·76 Cal. are developed; as this amount is somewhat less than the theoretical quantity, 14·15 Cal., for complete displacement of the ether from the oxonium compound by ethyl sulphide, it may be that here, too, the bromine is distributed between the sulphide and the ether.

T. H. P.

Catalytic Acceleration of the Esterification of Organic Acid by means of Glucinum Compounds. OTTO HAUSER and A. KLOTZ (*Chem. Zeit.*, 1913, **37**, 146).—Experiments on the solubility of glucinum acetate in various organic solvents have led the authors to the discovery that the rate of esterification of organic acids and alcohols can be considerably increased by the addition of glucinum acetate or hydroxide to the boiling mixture. The catalytic action of glucinum compounds is still more pronounced when the mixed vapours of the acid and alcohol are passed over the oxide heated at 310°. The authors claim that better yields are obtained by this process than by that of Sabatier (actually 70% and over), that there is no loss of catalyst, since the glucinum oxide after use can be regenerated by simple ignition, and that tertiary alcohols and acids of high molecular weight can be esterified in this manner. The following new esters have been prepared: tert.-*butyl* n-*octoate*, b. p. 241°; tert.-*amyl* n-*heptoate*, b. p. 137°, and tert.-*amyl* n-*octoate*, b. p. 229°. H. W.

Mechanism of the Action of Bromine on Chlorides of Fatty Acids. ARTHUR MICHAEL and ERWIN SCHARF (*Ber.*, 1913, **46**, 135—138).—When butyryl chloride, saturated with hydrogen bromide at 0°, is heated in sealed tubes at 100°, double decomposition takes place with the formation of butyryl bromide and hydrogen chloride. It is probable therefore that the formation of hydrogen chloride by the action of bromine on acyl chlorides is not due to the decomposition of a bromine additive product, formed from the enolic modification of the chloride, but is brought about by the direct action of the chloride with hydrogen bromide produced during the reaction. This is not in agreement with Lapworth's (T., 1904, **85**, 30) interpretation of the change.

Proof is further given that by the action of bromine on butyryl chloride in sunlight some quantity of the β-derivative as well as the α-derivative is formed. Hydrogen chloride and bromide in equal proportions are liberated on opening the tube. When the contents were converted into the ethyl ester, and hydrolysed with barium hydroxide, considerable quantities of crotonic acid derived from the β-ester were obtained. E. F. A.

Aliphatic Nitro-compounds. XIII. Preparation of α-Nitro-α-methylbutyric Acid. WILHELM STEINKOPF (*Ber.*, 1913, **46**, 98—100).—An unfinished attempt to prepare a tertiary nitrocarboxylic acid containing an asymmetric carbon atom.

[With HARRY GRÜNUPP and LEO HUG.]—A mixture of butanoneoxime with anhydrous hydrogen cyanide is kept in a closed flask for four to eight days at the ordinary temperature, and the excess of acid then removed in a vacuum; crystals of *α-hydroxylamino-α-methylbutyronitrile*, OH·NH·CMeEt·CN, m. p. 61·5°, are obtained. When this substance is oxidised by the cautious addition of an acidified solution of potassium permanganate, a blue *oil* (probably α-nitroso-α-methylbutyronitrile) is first formed, but disappears later with the production of *α-nitro-α-methylbutyronitrile*, NO_2·CMeEt·CN, an almost colourless oil, b. p. 87—88°/17 mm. Attempts to hydrolyse this to the corre-

sponding acid, or to convert it into an imino-ester hydrochloride were unsuccessful. D. F. T.

Action of Alkali Sulphites on the Ethylenic Acids. J. BOUGAULT and MOUCHEL-LA-FOSSE (*Compt. rend.*, 1913, **156**, 396—398).—It being known that, on adding benzoylacrylic acid to a solution of normal or sodium hydrogen sulphite, combination instantly takes place, giving the sodium salt of a saturated sulphonic acid (compare Bougault, *Ann. Chim. Phys.*, 1908, [viii], **15**, 299), the authors have compared the activity of different types of ethylenic acids in this reaction. A large number of ethylenic acids combine in this way with sodium hydrogen sulphite, giving acids of the type $CH_2R\cdot CH(SO_3Na)R'$, which are very soluble in water, and, on heating with aqueous sodium hydroxide to 160°, regenerate the original unsaturated acid. The more energetic is the acid and the more electronegative groups it contains, the more rapid is the fixation of the sodium hydrogen sulphite. Acids such as *cyclo*geranic, undecenoic, and oleic acids, and in general those with long, straight chains, do not combine with the sodium hydrogen sulphite even after prolonged heating. The reaction can be employed to estimate the amount of unsaturated acid in a mixture of saturated and unsaturated acids, and also permits of the separation of the saturated acid in a pure state. W. G.

The Salts of Rare Earths with Hydroxycarboxylic Acids. I. The Glycollates of the Rare Earths. GUSTAV JANTSCH and A. GRÜNKRAUT (*Zeitsch. anorg. Chem.*, 1913, **79**, 305—321).—The internally complex salts of rare earths with hydroxycarboxylic acids might be expected to differ more widely in solubility than the normal salts, and therefore to be suitable for the purpose of separation. It is found that the glycollates of the cerium group are anhydrous, and crystallise in crusts, whilst those of the yttrium group crystallise in needles with $2H_2O$. The yttrium salt is the least soluble, then follow the lanthanum, cerium, and praseodymium salts, which are almost equal, and then, in order, the neodymium, samarium, and gadolinium salts. The solutions exhibit the normal reactions, but conductivity determinations show that complexes are present.

Lanthanum hydroxide dissolves in a warm solution of glycollic acid, the solution at first remaining clear, but at a definite temperature, depending only on the concentration, the complex salt separates as a precipitate, $La(C_2H_3O_3)_3$. The praseodymium, neodymium, and samarium salts behave in the same manner.

Gadolinium glycollate, $Gd(C_2H_3O_3)_3,2H_2O$, crystallises without first forming an unstable solution, whilst the yttrium salt behaves like those mentioned above.

The fractionation of the earths from xenotime, previously freed from cerium, has been carried out by adding a solution of sodium glycollate to the hot solution of the mixed nitrates. After each addition, in order to overcome the unstable condition, the mixture is stirred vigorously for two hours at 80—90°. It is then filtered, and the filtrate is treated in similar manner. Successive fractions show a

progressive increase in the atomic weight, whilst the spectra show a concentration of neodymium and praseodymium in the last fractions.
C. H. D.

Succinic Semialdehyde [β-Aldehydopropionic Acid]. EDMOND E. BLAISE and E. CARRIÈRE (*Compt. rend.*, 1913, **156**, 239—241).—A reply to Harries (A., 1912, i, 827), in which the authors uphold the views already expressed by Carrière (A., 1912, i, 410) that β-aldehydopropionic acid changes spontaneously into a polymeride which is termolecular, and that the bimolecular compound, m. p. 147°, of Harries (*loc. cit.*) is the compound obtained by the elimination of $1H_2O$ from two molecules of the aldehyde.
W. G.

General Method for the Preparation of the Ammonium Salts of Organic Acids. EDWARD H. KEISER and L. MCMASTER (*Amer. Chem. J.*, 1913, **49**, 84—86).—On account of the hydrolytic action of water on the ammonium salts of organic acids, comparatively few of them have hitherto been prepared, and in the case of most dibasic acids only the ammonium hydrogen salts have been obtained. It has now been found that normal salts can be readily prepared by passing dry ammonia into a solution of the organic acid in ether or alcohol, or a mixture of the two. The salts are insoluble, and separate in the form of white precipitates. *Ammonium maleate, fumarate, mesaconate, citraconate, malonate,* and *phthalate* are described.
E. G.

Sebacates and Cacodylates of the Rare Earths. C. F. WHITTEMORE and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1913, **35**, 127—132; *Chem. News*, 1913, **107**, 75—77).—In an earlier paper (A., 1912, ii, 690) it was shown that yttrium can be separated quantitatively from the alkali metals by precipitation with ammonium sebacate. It has now been found that lanthanum and cerium can also be separated from the alkali metals in this way. The following salts are described: *lanthanum sebacate*, $[C_8H_{16}(CO_2)_2]_3La_2,2H_2O$; *praseodymium sebacate*,

$$[C_8H_{16}(CO_2)_2]_3Pr_2,2H_2O;$$

neodymium sebacate, $[C_8H_{16}(CO_2)_2]_3Nd_2,3H_2O$; *samarium sebacate*, $[C_8H_{16}(CO_2)_2]_3Sa_2,4H_2O$; *yttrium sebacate*,

$$[C_8H_{16}(CO_2)_2]_3Yr_2,4H_2O.$$

On fractionally precipitating a solution containing chiefly the chlorides of yttrium, dysprosium, and holmium with sodium cacodylate, it was found that yttrium tended to accumulate in the early fractions, and holmium and dysprosium in the later fractions. On boiling a mixture of hydroxides, consisting mainly of those of neodymium, samarium, and gadolinium, with cacodylic acid and fractionally crystallising the cacodylates from hot water, neodymium collected in the more soluble fractions, whilst nearly all the terbium and dysprosium remained in the least soluble portions. The following salts have been prepared: *praseodymium cacodylate*, $(AsMe_2O_2)_6Pr_2,16H_2O$; *yttrium cacodylate*, $(AsMe_2O_2)_6Yr_2,18H_2O$; *thulium cacodylate*,

$$(AsMe_2O_2)_6Tm_2,16H_2O.$$

Neodymium and samarium cacodylates have been described previously (A., 1912, i, 233).

The rare earth cacodylates readily form double salts with other salts, such as the chlorides, nitrates, and sulphates. The following are described: *lanthanum chloride cacodylate*,

$$2La(AsMe_2O_2)_3,LaCl_3,18H_2O;$$

cerium chloride cacodylate, $2Ce(AsMe_2O_2)_3,CeCl_3,18H_2O$; *cerium sulphate cacodylate*; and *neodymium chloride cacodylate*,

$$2Nd(AsMe_2O_2)_3,NdCl_3,18H_2O.$$

E. G.

The Action of *p*-Bromophenylhydrazine on Glycuronolactone. Guido Goldschmiedt and Ernst Zerner (*Ber.*, 1913, **46**, 113—115).—In reply to Jolles (this vol., i, 9), the authors maintain their previous statement (this vol., i, 9), that even with purified *p*-bromophenylhydrazine the test for glycuronic acid is so uncertain as to be of little practical value.

D. F. T.

Behaviour of Chloraloxime Towards Water and Alkalis. F. Carlo Palazzo and V. Egidi (*Gazzetta*, 1913, **43**, i, 57—69. Compare Palazzo, A., 1912, i, 946; Palazzo and Fazio, 1911, i, 421).—When Meyer's chloraloxime is kept for some days with ten times its weight of water, an acid solution is obtained, from which can be isolated a product having the composition of oximinoacetic acid; it has, however, an indefinite m. p., and is to be regarded as a mixture of two stereoisomerides. It differs from the oximinoacetic acid, m. p. 138°, already known, in yielding a red coloration with ferric chloride. When Meyer's chloraloxime is distilled, several liquid fractions, b. p. 65—85°/20—25 mm., are obtained, and also a portion, b. p. 85°/20 mm., which solidifies and has m. p. 56°. Even if carefully freed from the liquid form, the solid substance yields, when treated with water, a product similar to that given by the original mixture.

By the action of hydroxylamine hydrochloride on bromal hydrate, *bromaloxime* is obtained in acicular crystals, m. p. 115°; it has the composition and molecular weight required by the formula

$$CBr_3\cdot CH:NOH.$$

Oximinoacetic acid forms two *copper* salts, namely, a blue salt,

$$[OH\cdot N:CH\cdot CO_2]_2Cu,2H_2O,$$

and a dark green salt of the probable composition $\begin{matrix} CH:NO \\ | \\ CO_2 \end{matrix}\!\!>\!Cu.$

R. V. S.

Inosite-phosphoric Acid. Anton Richard Rose (*Biochem. Bull.*, 1912, **2**, 21—49).—A useful review with bibliography on the subject.

W. D. H.

Syntheses of Alkylgalactosides by means of Emulsin, β-Propylgalactoside and β-Benzyl Galactoside. Émile Bourquelot, Henri Hérissey, and Marc Bridel (*Compt. rend.*, 1913, **156**, 330—332).—The two galactosides have been prepared from galactose and the corresponding alcohols under the influence of emulsin by the method previously described (A., 1912, i, 946).

β-Propylgalactoside, m. p. 105—106° (corr.), $[\alpha]_D - 8{\cdot}86°$, crystallises in long, white needles, having a slightly bitter taste. It is not hygroscopic, but is very soluble in alcohol and water, and gives a slight reduction with Fehling's solution.

β-Benzylgalactoside, m. p. 100—101°, $[\alpha]_D - 25{\cdot}05°$, crystallises in long, white needles, having a disagreeable bitter taste. It is not hygroscopic, and gives but traces of reduction with Fehling's solution. Both of these galactosides are readily hydrolysed by emulsin in aqueous solution. W. G.

Photochemical Synthesis of Carbohydrates. WALTHER LÖB (*Biochem. Zeitsch.*, 1913, **48**, 257—258).—A reply to Stoklasa, Šebor, and Zdobnický (this vol., i, 18). S. B. S.

Cellulose. C. PIEST (*Zeitsch. angew. Chem.*, 1913, **26**, 24—30).—The viscosity of a solution of a cellulose nitrate decreases with time and, generally, a deposit settles on the bottom of the vessel containing the solution. Experiments have been made which show that the decrease in the viscosity is not due to the separation of this deposit from the solution.

It has been stated previously that, a diminution in the viscosity of a solution of cellulose nitrate is probably due to the presence of nitrates of oxycelluloses. It is shown now that if a viscous solution of a cellulose nitrate be mixed with a less viscous solution of a nitrate of a highly bleached cotton wool the viscosity of the mixture is considerably less than the calculated value, although if two solutions of the same cellulose nitrate, but of different concentrations (and, therefore, different viscosities), be mixed, the mixture has a viscosity which is very close to the calculated value.

Cellulose, when treated with oxidising agents, is known to yield oxycelluloses, the part soluble in sodium hydroxide solution being termed β-oxycellulose, whilst the insoluble portion is called α-oxycellulose. The results of numerous trials, based on determinations of the "copper value" and viscosity of a standard solution in a cuprammonium solution by Ost's method (compare A., 1911, i, 838), show that α-oxycellulose, when carefully freed from the degradation products grouped under the name β-oxycellulose, is chemically identical with normal cellulose, and differs from it only in that the fibres are much shorter and finer, owing to the attack of the oxidising agent.

It is also shown that the products of the action of acids on cellulose ("hydrocellulose"), or of a hot 30% solution of sodium hydroxide ("alkalised cellulose"; compare Ost and Katayama, A., 1912, i, 680), contain a portion insoluble in sodium hydroxide solutions which is unattacked cellulose. W. H. G.

Preparation of Higher Aliphatic Chlorinated Amines. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1913, **46**, 228—231. Compare von Braun and Müller, A., 1907, i, 28).—The bis-imidochlorides of the type $CPhCl{:}N{\cdot}[CH_2]_n{\cdot}N{:}CPhCl$, obtained by the action of phosphorus pentachloride on the corresponding dibenzoylated diamine, when distilled undergo decomposition mainly into benzonitrile and the

dichloride, but to a slight extent a product $Cl\cdot[CH_2]_n\cdot N:CPhCl$, in which only one of the phenyl radicles has been eliminated, is obtained (compare von Braun and Danziger, A., 1912, i, 597). As the latter class of substance on hydrolysis would give rise to chloroamines, the method might prove valuable if the yield of the second class of product could be increased.

It is now found that at very low pressures the desired decomposition at one end of the chain is greatly favoured.

$\alpha\zeta$-Di-iodohexane reacts with potassium cyanide, giving suberonitrile, $CN\cdot[CH_2]_6\cdot CN$, b. p. 176—178°/11 mm., which by successive reduction (by sodium and alcohol) and benzoylation is converted into *αθ-dibenzoyldiamino-octane*, $NHBz\cdot[CH_2]_8\cdot NHBz$. When the last substance is carefully fused with a bimolecular proportion of phosphorus pentachloride and the resultant mixture warmed under a pressure of 0·1 mm., there distils into the receiver, which is cooled by liquid air, a mixture of benzonitrile, αθ-dichloro-octane, and *θ-chlorobenzo-octylamide*, $COPh\cdot NH\cdot[CH_2]_8\cdot Cl$, colourless leaflets, m. p. 65°, the last of which is most conveniently purified by means of its *compound* with calcium chloride. θ-Chlorobenzo-octylamide is hydrolysed by hydrochloric acid at 150°, with the formation of *θ-chloro-octylamine*; *hydrochloride*, hygroscopic; *platinichloride*, m. p. 193—194° (decomp.), sparingly soluble. The base on treating its hydrochloride with alkali easily undergoes intramolecular change to a *base*, $C_8H_{17}N$, with an odour resembling pyridine; yellow *platinichloride*, m. p. 197°.

In an analogous manner by the distillation of dibenzoyldiaminoheptane and of dibenzoyldiaminododecane with phosphorus pentachloride under a pressure of 0·1 mm., *η-chlorobenzoheptylamide*, $Cl\cdot[CH_2]_7\cdot NHBz$, and *μ-chlorobenzododecylamide*, $Cl\cdot[CH_2]_{12}\cdot NHBz$, m. p. 65°, can be obtained in fair quantity.

The yields were 40%, 30%, and 30% of the theoretical in the heptane, octane, and dodecane series respectively. D. F. T.

Dibromides of Tertiary Amines. VLADIMIR V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1894—1905).—With a view to the comparison of dibromides obtained from tertiary amines with oxonium and thionium dibromides (compare this vol., i, 245), the author has investigated their solubilities in various solvents, their molecular weights, and their chemical and thermochemical relations.

A general parallelism exists between the solubility of trimethylamine dibromide and those of oxonium and thionium dibromides. Also in freezing acetic acid, trimethylamine dibromide has the molecular weight corresponding with the simple formula NMe_3Br_2, and is hence completely analogous to oxonium and thionium compounds in this respect (compare Hantzsch and Graf, A., 1905, i, 575).

Amine dibromides are somewhat more stable than the oxonium compounds towards moisture and are decomposed by ethyl alcohol, yielding hydrogen and ethyl bromides. When treated with excess of bromine, dibromides of amines are converted into new compounds, which possess peculiar properties distinguishing them from dibromides and represent a different class of perbromides.

The heat of formation of tripropylamine dibromide from its constituents is 39·72 Cal. per gram-mol., and that of tri*iso*amylamine dibromide, 38·76 Cal.; the carbon tetrachloride employed as solvent is without influence on the amount of heat developed (see this vol., i, 245).

Thermochemical investigation of the interaction of diethyloxonium dibromide or diethylthionium dibromide and tripropylamine in carbon tetrachloride solution shows that the tertiary amine displaces the ether or ethyl sulphide completely from oxonium or thionium compounds.

Ether has no action on diethyloxonium dibromide, and ethyl sulphide none on diethylsulphonium dibromide, but tertiary amine dibromides react energetically with tertiary amines, forming compounds separating from carbon tetrachloride in a felted mass of slender, pale yellow needles. The following thermochemical data were obtained:

$$2NPr_3Br_2 + NPr_3 = 23{\cdot}6 \text{ Cal.}$$

and $2N(C_5H_{11})_3Br_2 + N(C_5H_{11})_3 = 22{\cdot}9$ Cal. The compounds formed in this way are being investigated further.

Neither the structure suggested by Hantzsch (A., 1905, i, 576) nor that given by Cain (A., 1905, i, 747) for these amine dibromides seems to explain the reactions better than the simple formula.

T. H. P.

Preparation of Oxan and the Properties of Salts of α- and β-Oxan. ALEXANDER P. LIDOV (*J. Amer. Chem. Soc.*, 1913, 35, 132—134. Compare Abstr., 1912, i, 541).—Oxan is obtained most readily by the action of nitric oxide or nitrous oxide on charcoal at 150—300°. α-Oxan, O·C⋮N, is a stable gas and is not affected by hot platinised asbestos, whilst β-oxan, O·N⋮C, is rapidly decomposed under these conditions. The sodium salt of α-oxan is stable when heated, whilst that of β-oxan decomposes explosively. The silver salt of β-oxan is pale yellow and darkens rapidly on exposure to light; that of α-oxan is white and is less susceptible to the action of light. The iron and calcium salts are also described. The sodium salt of α-oxan gives a white precipitate with manganous chloride or aluminium chloride, whilst that of β-oxan does not yield a precipitate. The salts of α- and β-oxan gradually cease to evolve gas, and this is probably due to polymerisation taking place.

E. G.

Action of Sulphuric Acid on Dicyanodiamide. HJ. LIDHOLM (*Ber.*, 1913, **46**, 156—160).—The interaction of dicyanodiamide with acids to form guanylcarbamide has been studied quantitatively and shown to be a bimolecular reaction. Guanylcarbamide is a sufficiently strong base to be titrated with sulphuric acid and methyl-orange.

Concentrated sulphuric acid acts on dicyanodiamide, liberating carbon dioxide and ammonia and forming guanidine. Guanylcarbamide is decomposed in a similar manner. These observations confirm the structure of dicyanodiamide as guanidinoformonitrile,

$$NH{:}C(NH_2){\cdot}NH{\cdot}CN.$$

E. F. A.

The Tautomerism of Fulminic Acid. F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 713—719. Compare A., 1907, i, 298, 489; 1909, i, 776).—The author's work on this subject has led him to conclusions similar to those of Ley and Kissel (A., 1899, ii, 485), according to which fulminic acid is to be regarded as a tautomeric substance related to the pseudo-acids. In the aqueous solution of fulminic acid, there is equilibrium between various saturated and unsaturated desmotropic forms. In the present paper this opinion is developed, and a new argument in its favour is drawn from the behaviour of sodium fulminate with azoimide, for in this reaction the fulminic acid reacts sometimes as carbyloxime and sometimes in the desmotropic form of formonitryl oxide, HC⋮N:O. The products of the reaction are hydroxytetrazole (I), m. p. 145°, and *iso*oxytetrazole (II),

$$\text{(I.)}\quad \begin{array}{l}\text{HC—N·OH}\\ \dot{\text{N}}\text{·N:}\dot{\text{N}}\end{array} \qquad\qquad \text{(II.)}\quad \begin{array}{l}\text{N——CH}\\ \dot{\text{N}}\text{·NH·}\dot{\text{N}}\text{:O}\end{array}$$

m. p. 156°, and the relative proportions in which these two substances are formed depend on the temperature at which the reaction proceeds.

R. V. S.

Catalysis. XIV. Reversible Addition of Alcohols to Nitriles Catalysed by Ethoxides. I. ELI K. MARSHALL, jun., and SOLOMON F. ACREE [and, in part, C. N. MYERS] (*Amer. Chem. J.*, 1913, **49**, 127—158).—A study has been made of the addition of alcohols to nitriles in presence of ethoxides as catalysts. It has been found that nitriles unite with ethyl alcohol in presence of sodium, potassium or lithium ethoxide, and that in every case the reaction is reversible. The percentage of imino-ester present when equilibrium is attained is the same whether the reaction is started with the nitrile or the imino-ester. The equilibrium point varies widely with the different compounds, the percentages of imino-ester formed with certain nitriles being as follows: butyronitrile, 0·90; propionitrile, 1·75; acetonitrile, 2·50; *p*-toluonitrile, 6·8; benzonitrile, 14·0; *p*-bromobenzonitrile, 27·2; *m*-bromobenzonitrile, 38·0; *p*-nitrobenzonitrile, 62·0; *m*-nitrobenzonitrile, 78·0; di*iso*amylcyanoamide, 98·0. In some cases, the equilibrium point varies considerably with changes in the concentration of the nitrile and the ethoxide, but in other cases shows but little fluctuation. Different ethoxides catalyse the reaction with different velocities, and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, *p*-nitrobenzonitrile reacting very rapidly, whilst *o*-toluonitrile scarcely unites with alcohol at all.

Certain experiments are described which show that the velocity of reaction can be expressed as a function of both the ethoxide ions and the non-ionised ethoxide.

E. G.

Nitrile of Fumaric Acid and the Preparation of Methyl Maleate. EDWARD H. KEISER and L. MCMASTER (*Amer. Chem. J.*, 1913, **49**, 81—84).—Keiser and Kessler (A., 1911, i, 949) have shown that fumaronitrile can be prepared by heating fumaramide with phosphoric oxide. It has now been found that the nitrile can be

converted into fumaramide by treating it with an alkaline solution of hydrogen peroxide.

Methyl maleate, which has only been obtained previously by the action of methyl iodide on silver maleate, has now been prepared by heating a mixture of maleic acid, methyl alcohol, and sulphuric acid under a reflux condenser. When the ester is left with solution of ammonia for several days, it gradually dissolves, and on evaporation a yellow viscous mass is obtained which is probably maleamide.

E. G.

The Action of Light on Pigments. II. The Composition of Turnbull's Blue. ALEXANDER EIBNER and L. GERSTACKER (*Chem. Zeit.*, 1913, **37**, 137—139, 178—179, 195—197).—As a result of their experiments, the authors come to the conclusion that freshly prepared Turnbull's blue is not identical with Paris blue, but is a derivative of ferricyanic acid. It is not the most labile of the ferricyanides of the heavy metals, those of ferric iron, zinc, cadmium, lead, and copper being less stable. On long-continued washing or heating, a change takes place between the constituents of Turnbull's blue, resulting in the reduction of the ferricyanogen and oxidation of the ferrous radicle. The final result of such treatment is identical with Paris blue, the velocity of change depending on the conditions.

T. S. P.

Spirocyclane, its Synthesis and Behaviour on Catalytic Reduction. NICOLAI D. ZELINSKI (*Ber.*, 1913, **46**, 160—172; *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1873—1884).—The hydrocarbon formed by the action of zinc dust and alcohol on the tetrabromide of pentaerythritol has been regarded by Gustavson (A., 1896, i, 669) as vinyltrimethylene. Reasons are now given for formulating the compound as spirocyclane, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\|\\CH_2\end{matrix}$. The only other possible constitution is that of methylene*cyclo*butane.

The hydrocarbon is very readily and completely reduced in contact with nickelised asbestos and hydrogen at about 100°. No condensation product is formed, the gaseous mixture consisting entirely of saturated hydrocarbons. This behaviour eliminates any other constitution than that of the spirocyclane.

[With V. KRAVEC.]—This is confirmed by effecting the synthesis of spirocyclane by closing the two trimethylene rings one after the other.

By the action at 0° of hydrogen bromide on pentaerythritol, the *dibromohydrin*, $C(CH_2Br)_2(CH_2{\cdot}OH)_2$, is obtained. This crystallises in well formed needles, m. p. 112°; the *diacetyl* derivative has b. p. 185°/13 mm.

When reduced with zinc dust, the *diacetate* of *dimethylolcyclopropane* is obtained, b. p. 115°/15 mm. The *glycol*,

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C(CH_2{\cdot}OH)_2,$$

has b. p. 126—127°/16 mm., D_4^{20} 1·0794, $n^{20\cdot5}$ 1·4705. When oxidised with permanganate, it yields *cyclo*propane-1 : 1-dicarboxylic acid.

Phosphorus tribromide converts the glycol into *dibromodimethylcyclopropane*, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\cdot(CH_2Br)_2$, b. p. 72—74°/13 mm., D_4^{20} 1·8022, n = 1·534. In addition, a tribromide resulting from the opening of the *cyclo*propane ring is formed.

On reduction of the dibromide, spirocyclane is obtained, b. p. 40—41·5°, D_4^{20} 0·7266, n = 1·4120, in agreement with earlier values.

[With B. SCHTSCHERBAK.]—When a mixture of spirocyclane and hydrogen is passed over platinum black at 70°, a mixture of ethyl*cyclo*propane and pentane is formed. Using palladium black in the cold, it is possible to restrict the reduction entirely to one ring and obtain ethyl*cyclo*propane alone. In order to reduce the second ring, nickel must be used as catalyst—a temperature of 200° is necessary before *iso*pentane is obtained. The reduction of spirocyclane thus takes place in two stages and selective catalysts are required. Nickel in the cold reduces it only to ethyl*cyclo*propane. E. F. A.

Preparation of the Three Cymenes (Methyl*iso*propylbenzenes) and Three Menthanes (Methyl*iso*propyl*cyclo*hexanes). PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 184—187. Compare Sabatier and Senderens, A., 1901, i, 459).—Starting from the three tolyldimethylcarbinols, $C_6H_4Me\cdot CMe_2\cdot OH$, the authors have prepared the three corresponding cymenes and menthanes, and examined their physical properties. The three carbinols were prepared either (1) by the action of magnesium methyl iodide on the ethyl *o*-, *m*-, and *p*-toluates, or on the three tolyl methyl ketones, or (2) by the action of acetone on the three magnesium tolyl bromides. The vapours of the three carbinols were completely dehydrated under the influence of thorium oxide at 350°, giving respectively *o*-, *m*-, and *p*-β-allyltoluene, $C_6H_4Me\cdot CMe\!:\!CH_2$, which by the action of slightly activated nickel at 200—220° yielded the corresponding cymenes. These substances underwent further hydrogenation when passed in the form of vapour over activated nickel at 170—180°, and the corresponding menthanes were obtained, all of which have been previously described. In certain cases the values of the physical constants now obtained differ from those previously given by other authors, namely, *o*-β-allyltoluene has b. p. 175°, D_0^{15} 0·9181, n_D^{15} 1·521 (compare Tiffeneau, A., 1907, i, 305).

o-Cymene has b. p. 175° (corr.), D_0^0 0·8902, n_D^{22} 1·501 (compare Sprinkmeyer, 1901, i, 519).

o-Menthane, b. p. 171° (corr.), D_0^0 0·8326, D_0^{21} 0·8135, n_D^{21} 1·447 (compare Kay and Perkin, T., 1905, **87**, 1066).

r-*m*-Menthane, b. p. 166—167° (corr.), D_0^{24} 0·7968, n_D^{24} 1·440.

d-*m*-Menthane was obtained by the hydrogenation of natural *d*-sylvestrene at 200° by activated nickel, and has b. p. 167—168°, D_0^0 0·8235, D_0^{23} 0·8116, n_D^{23} 1·446, $[\alpha]_D^{23}$ +1·60° (compare Knoevenagel, A., 1897, i, 610).

The para-isomeride has b. p. 167—168° (corr.), D_0^0 0·8134, D_0^{25} 0·8028, n_D^{25} 1·440 (compare Sabatier and Senderens, *loc. cit.*). W. G.

Systems Formed by Chloro- and Nitro-toluenes with Antimony Trihaloids. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1939—1963).—*o*-, *m*-, and *p*-Chlorotoluenes melt at −36·2°

(Haase, A., 1892, ii, 357, gave $-34°$), $-47·8°$, and $6·2°$ (Haase, *loc. cit.*, gave $7·4°$) respectively.

With antimony trichloride, *o*-chlorotoluene forms the compound, $SbCl_3,C_6H_4MeCl$, crystallising in long plates or needles, m. p. 3°, and the eutectic points and compositions are (1) 37·5° and

$$SbCl_3,24·1C_6H_4MeCl,$$

and (2) $-0·5°$ and $SbCl_3,1·95C_6H_4MeCl$. *m*-Chlorotoluene gives the compound, $SbCl_3,C_6H_4MeCl$, which is much less stable than that formed by the ortho-derivative and decomposes before melting; the eutectic points are (1) $-14°$, $SbCl_3,2·7C_6H_4MeCl$, and (2) $-49°$, $SbCl_3,24·1C_6H_4MeCl$. *p*-Chlorotoluene and antimony trichloride form no compound, the diagram showing only one eutectic point at $-7·5°$, corresponding with $SbCl_3,2·3C_6H_4MeCl$.

With antimony tribromide, none of the chlorotoluenes form compounds. The eutectic points and the corresponding compositions are for the ortho-compound, $-38·5°$ and $SbBr_3,23·8C_6H_4MeCl$; for the meta-compound, $-50°$ and $SbBr_3,32·3C_6H_4MeCl$, and for the para-compound, 2·5° and $SbBr_3,9·4C_6H_4MeCl$.

o-Nitrotoluene has m. p. $-8·5°$ (Knoevenagel, A., 1907, i, 202, gave $-9·4°$, and Ostromisslensky, A., 1907, i, 120, $-10·56°$) for the more stable α-modification and $-4°$ for the less stable β-form; the solutions in antimony trihaloid always correspond with the α-compound. The meta- and para-isomerides melt at 16° and 52·5° respectively.

o-Nitrotoluene and antimony trichloride give the compound

$$SbCl_3,C_6H_4Me·NO_2,$$

crystallising in slender needles, m. p. 34·5°; the eutectic points are $-18·5°$, corresponding with $SbCl_3,7·28C_6H_4Me·NO_2$, and 27·5° with $SbCl_3,0·56C_6H_4Me·NO_2$. *m*-Nitrotoluene and antimony chloride form a compound, which apparently melts at a higher temperature than the corresponding para-compound, but could not be obtained crystalline.

p-Nitrotoluene and antimony chloride form a compound

$$SbCl_3,C_6H_4Me·NO_2,$$

which crystallises with difficulty; the eutectic points and compositions are: (1) 7·5° and $SbCl_3,1·55C_6H_4Me·NO_2$, and (2) 3° and

$$SbCl_3,0·76C_6H_4Me·NO_2.$$

With antimony tribromide, *o*-nitrotoluene forms the compound $SbBr_3,C_6H_4Me·NO_2$, crystallising in needles, m. p. 32° (decomp.), isomorphous with those of the corresponding compound of antimony trichloride. The system exhibits one eutectic point, $-13·5°$, corresponding with $SbBr_3,10·8C_6H_4Me·NO_2$, and one transition point, 31°, corresponding with $SbBr_3,1·3C_6H_4Me·NO_2$. *m*-Nitrotoluene and antimony tribromide form no compound, the system showing only one eutectic point, $-9°$, corresponding with $SbBr_3,2C_6H_4Me·NO_2$. The para-derivative also forms no compound with the tribromide, the diagram consisting of two curves meeting at the eutectic point, 16°, for which the composition is $SbBr_3,1·3C_6H_4Me·NO_2$.

These results are discussed in relation to those obtained with benzene and its other substituted derivatives (*loc. cit.*). T. H. P.

Δ^1-Dihydronaphthalene. FRITZ STRAUS and LEO LEMMEL (*Ber.*, 1913, **46**, 232—241).—If Δ^2-dihydronaphthalene, which was obtained

by Bamberger and Lodter (A., 1888, 292; 1896, i, 99) by the action of sodium and ethyl alcohol on naphthalene, is heated with an alcoholic solution of sodium ethoxide, it quantitatively undergoes isomeric change into the hitherto unknown Δ^1-dihydronaphthalene.

Crude Δ^2-dihydronaphthalene was purified by shaking in ethereal solution with an aqueous solution of mercuric acetate; the crystalline mercury compound, after washing with ether, was dissolved in benzene, when a slight insoluble residue was obtained, apparently of the mercury compound of Δ^1-dihydronaphthalene, due to a trace of this hydrocarbon in the crude starting substance. The pure mercury compound, m. p. 119—120°, obtained on evaporation of the solution, when decomposed with a 30% solution of hydrochloric acid, gave pure Δ^2-dihydronaphthalene, leaflets, m. p. 24·5—25°, b. p. 94·5°/17 mm., which on heating for eight hours at 140—150° with sodium ethoxide in alcoholic solution was isomerised into *Δ^1-dihydronaphthalene*, b. p. 84—85°/12 mm., m. p. −8° to −7°, an unpleasant-smelling liquid which immediately decolorises permanganate; when shaken with mercuric acetate, it is slowly converted into a white *mercury* derivative, which is insoluble in benzene, and does not melt below 250°; the *dibromide*, colourless crystals, m. p. 70—71°, is quite distinct from that (m. p. 71·5—72°) of the Δ^2-isomeride, and when boiled with alcoholic potassium hydroxide gives an oily *substance* of characteristic odour, together with a little naphthalene.

When an emulsion of Δ^1-dihydronaphthalene in water is oxidised by the gradual addition of concentrated potassium permanganate solution, *o*-carboxyphenylpropionic acid is obtained, together with a quantity of a pungent *substance* of low m. p. The further reduction of Δ^1-dihydronaphthalene can be accomplished by the addition of its alcoholic solution to finely-divided sodium, the product being tetrahydronaphthalene.

The above method of formation of Δ^1-dihydronaphthalene disposes of the difficulty of reconciling the reduction of naphthalene through Δ^2-dihydronaphthalene to tetrahydronaphthalene with the behaviour of the analogous allylbenzene and propenylbenzene, only the latter of which is reducible by sodium and alcohol to a saturated homologue of benzene (Klages, A., 1903, i, 19, 329; 1904, i, 567); according to this, Δ^2-dihydronaphthalene should not be directly reducible. The preparation of tetrahydronaphthalene by Bamberger and Kitschelt (A., 1890, 1146) is to be attributed to the reduction occurring by the stages

$$C_6H_4{<}\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\cdot CH\\ ||\\ CH_2\cdot CH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH{=}CH\\ |\\ CH_2\cdot CH_2\end{matrix} \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}$$

D. F. T.

Triphenylmethyl. XXII. Ethers or Oxides in the Triphenylmethane Series. Moses Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 200—210).—It is well known that diarylcarbinols can be converted into the corresponding ethers or oxides by heating them either alone or in presence of a dehydrating agent. A few oxides of the triaryl-

carbinols have also been reported in the literature, but the results of the present work show that most of the compounds thus designated were not in reality triarylmethyl ethers.

A general method is now described for the preparation of triarylmethyl ethers. These compounds are as stable as the peroxides, are not affected by exposure to the air, or by heating them to temperatures below their m. p.; they are not decomposed by water or dilute alkali hydroxide, even at 100°, but are hydrolysed when boiled with dilute acids, alcohol, acetic acid, or acetyl chloride.

When triphenylmethyl chloride is treated with silver oxide, oxidation takes place with formation of diphenylquinomethane and other products, but the ether is not obtained. If triphenylmethyl chloride is shaken with zinc oxide and ether in sealed tubes, it is reduced quantitatively to triphenylmethane, and this reaction furnishes a simple and rapid method for preparing the hydrocarbon. The oxides of cadmium, lead, nickel, cobalt, and magnesium do not react with triphenylmethyl chloride. When, however, a triarylmethyl chloride dissolved in a dry solvent, such as benzene, ether, carbon disulphide, or chloroform, is heated on the water-bath with mercuric oxide, the corresponding triarylmethyl ether is readily obtained in a good yield.

Triphenylmethyl ether, $CPh_3\cdot O\cdot CPh_3$, m. p. 235—237° (decomp.), forms white crystals, and is soluble in about 25 parts of benzene at the ordinary temperature, or in 5 parts of boiling benzene; 1 gram dissolves in 11 c.c. of carbon disulphide or in 325 c.c. of ether.

Phenylfluorene ether, $\left(\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CPh\right)_2O$, m. p. 232—233°, forms colourless crystals, and is soluble in about 6·5 parts of benzene or 100 parts of ether; it is readily converted into the peroxide, m. p. 193° (Gomberg and Cone, A., 1906, i, 822). The compound obtained by Kliegl (A., 1905, i, 187) by the action of acetic and sulphuric acids on phenylfluorenol is not identical with the ether now described.

Phenylxanthenol ether, $\left(O\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CPh\right)_2O$, m. p. 250—252°, forms pale yellowish-pink crystals, and is soluble to the extent of 1 gram in 12 c.c. of cold, or 5 c.c. of hot, benzene, or in 160 c.c. of ether.

p-*Methoxytriphenylmethyl ether*, m. p. 212°, is soluble to the extent of 1 gram in 25 c.c. of cold benzene.

p-*Acetoxytriphenylmethyl chloride*, m. p. 85—86°, obtained by the action of hydrogen chloride on a solution of the carbinol in benzene, forms white crystals; when treated with mercuric oxide, it is converted into p-*acetoxytriphenylmethyl ether*, m. p. 123—124° (decomp.), which crystallises in white needles, and is not identical with the substance to which this constitution was assigned by Bistrzycki and Herbst (A., 1901, i, 702); the latter was probably the carbinol as suggested by Auwers and Schröter (A., 1903, i, 821).

Another method has also been devised for preparing triarylmethyl ethers. When triphenylmethyl carbonate is heated under certain conditions, carbon dioxide is evolved and a nearly quantitative yield of triphenylmethyl ether is produced. The details of this method will be published subsequently.

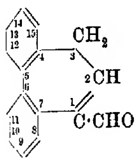
E. G.

Triphenylmethyl Ether. MOSES GOMBERG (*Ber.*, 1913, **46**, 225—228).—Although *triphenylmethyl ether* is not obtained in the action of silver oxide on triphenylmethyl chloride (compare Schlenk, this vol., i, 34), the application of mercuric oxide gives an almost quantitative yield of this substance (m. p. 235—237°). The reaction with mercuric oxide is a general one for the production of triarylmethyl ethers. Triphenylmethyl carbonate (m. p. 205—210°) when heated with copper as a catalyst to 140°, also decomposes into triphenylmethyl ether and carbon dioxide.

The opinion is expressed that the behaviour of triphenylmethyl and its analogues is best explained by an equilibrium between the three structures represented by the tervalent carbon, the hexaphenylethane, and Jacobson's (A., 1905, i, 186) formulæ.

D. F. T.

Synthesis of Pyrene. RICHARD WEITZENBÖCK (*Monatsh.*, 1913, **34**, 193—223).—Two schemes for the synthesis of pyrene have been followed. The first, which should have led to the preparation of diphenyl-2 : 2′-diacetaldehyde, which might have condensed in a manner analogous to the formation of β-phenylnaphthalene from phenylacetaldehyde (Auwers and Keil, A., 1904, i, 26), was unsuccessful. The tetramethylacetal of the dialdehyde was obtained, but on hydrolysis it gave 4 : 5 : 6 : 7-dibenzo-$\Delta^{1:4:6}$-*cyclo*heptatriene-2-aldehyde (annexed formula), the ready closing of the seven-membered ring recalling the formation of 2-imino-1-cyano-4 : 5 : 6 : 7-dibenzo-$\Delta^{4:6}$-*cyclo*heptadiene from diphenyl-2 : 2′-diacetonitrile (Kenner and Turner, T., 1911, **99**, 2104).



The other scheme was analogous to the preparation of 2 : 8-dihydroxychrysene from $\beta\gamma$-diphenyl-$\alpha\delta$-dihydromuconic acid (Beschke, A., 1911, i, 874), and consisted in the condensation of diphenyl-2 : 2′-diacetic acid to dihydroxypyrene which could be reduced by means of zinc dust or hydriodic acid and red phosphorus.

Scheme A.—It was first attempted to prepare diphenyl-2 : 2′-diacrylic acid by the distillation of *methyl* o-*iodocinnamate*, white needles, m. p. 40°, b. p. 300—310°, with copper, but the decomposition proceeded to the formation of phenanthrene. The ethyl ester could not be obtained pure, and gave still worse results. The acid was obtained, however, by Perkin's synthesis on 2 : 2′-dialdehydodiphenyl (compare Mayer, A., 1911, i, 870), being accompanied by the lactone of diphenyl-2-carbinol-2′-carboxylic acid (Kenner and Turner, *loc. cit.*), and was converted into the *diamide*, $C_{18}H_{16}O_2N_2$, white needles, by means of thionyl chloride and ammonia.

A better way to arrive at diphenyl-2 : 2′-diacetaldehyde was sought in the application of Weerman's method (A., 1907, i, 132) to the *amide* of o-*iodocinnamic acid*. This was obtained by the action of thionyl chloride and ammonia on the acid, in light brown, quadratic leaflets, m. p. 204—205°, the crude chloride having m. p. 63—64°. When treated with sodium hypochlorite in methyl alcohol, *methyl*

o-*iodostyrylcarbamate*, $C_6H_4I\cdot CH\colon CH\cdot NH\cdot CO_2Me$, was obtained in colourless leaflets, m. p. 128—130°, which on hydrolysis gave o-*iodophenylacetaldehyde*, C_8H_7OI, in pleasant smelling, white needles, m. p. 35—36°. When heated with copper, extensive decomposition took place, which was also the case with the *phenylbenzylhydrazone*,

$$C_{21}H_{19}N_2I,$$

stout, colourless needles, m. p. 104—105°. However, the *dimethylacetal*, $C_{10}H_{13}O_2I$, which was obtained by Fischer and Hoffa's method (A., 1898, i, 659) as a colourless, mobile oil, b. p. 144°/19 mm., gave a good yield of diphenyl-2 : 2′-diacetaldehyde,

$$C_{12}H_8\cdot[CH_2\cdot CH(OMe)_2]_2,$$

in the form of a viscid, yellow oil, b. p. 210—211°/13 mm. On hydrolysis, an unsaturated aldehyde was obtained, in white, pleasant smelling needles, m. p. 108—109°, which gave phenanthraquinone on oxidation with chromic acid, and is, therefore, to be regarded as 4 : 5 : 6 : 7-*dibenzo*-$\Delta^{1:4:6}$-cyclo*heptatriene*-1-*aldehyde*, rather than as phenanthryl-4-acetaldehyde. It gives a stable *dibromide*, $C_{16}H_{12}OBr_2$, in colourless needles, m. p. 133° (decomp.).

Scheme B.—Diphenyl-2 : 2′-diacetonitrile was hydrolysed by means of concentrated hydrochloric acid at 130—140° (compare Kenner and Turner, *loc. cit.*), and the acid was dehydrated with zinc chloride or, better, converted into the chloride with thionyl chloride and then condensed with aluminium chloride. The impure, reddish hydroxy-product gave pyrene when distilled with zinc dust or heated with hydriodic acid and red phosphorus at 200°. An attempt to convert dibromoditolyl into the nitrile by Mann's method for phenylacetonitrile (A., 1881, 1034) resulted in the formation of Kenner and Turner's 2-imino-1-cyano-4 : 5 : 6 : 7-dibenzo-$\Delta^{4:6}$-*cyclo*heptadiene. J. C. W.

Quaternary Salts of Alkylideneamines and a General Method of Converting Primary into Secondary Amines. HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, 395, 362—377).—The formation of a quaternary ammonium salt by the addition of an alkyl iodide to an alkylideneamine is practicable, but the product is often contaminated by other substances formed by (i) the dissociation of the salt into its generators, (ii) heterospasis (Decker and Fellenberg, A., 1909, i, 116), (iii) intramolecular change, ring formation, or polymerisation of the salt.

Quaternary alkylideneammonium iodides are decomposed by water or alcohol in the sense of the equation :

$$CHR''\colon NRR'I + H_2O = R''\cdot CHO + NHRR' + HI,$$

whereby a very satisfactory method is secured of converting primary into secondary amines without any possibility of the formation of the tertiary amines or the quaternary salt. The yield of the secondary amine is usually more than 75%, being less, however, in the case of primary aromatic amines containing the amino-group in the nucleus.

β-Phenylethylamine reacts with benzaldehyde and with vanillin on the water-bath to form β-*phenylethylbenzylideneamine*,

$$CH_2Ph\cdot CH_2\cdot N\colon CHPh,$$

m. p. 33—34°, colourless prisms, and β-*phenylethylvanillylidenea in*

m. p. 108—109°, leaflets, respectively. The former and methyl iodide at 100° yield an additive compound which is decomposed by boiling 95% alcohol into benzaldehyde and *β-phenylethylmethylamine h driodide*, $CH_2Ph\cdot CH_2\cdot NHMe,HI$, m. p. 113—115°. The base, which is also produced by heating β-phenylethylglycine above its m. p., forms a *hydrochloride*, m. p. 156—157° (decomp.), *platinichloride*, m. p. 225—226° (decomp.), and *picrate*, m. p. 141—143°. β-Phenylethylethylamine, prepared in a similar manner, forms a *hydriodide*, m. p. 166—168°. Methyl-*p*-toluidine, prepared in a similar manner from benzylidene-*p*-toluidine or heptylidene-*p*-toluidine, forms a *hydriodide*, m. p. 134—137°, pale yellow leaflets, and a *picrate*, m. p. 130—132° (decomp.), which is very sparingly soluble in benzene. Ethylaniline, methylaniline, and methyl*iso*butylamine have also been prepared by this method. C. S.

The Nitro-derivatives of *o*-Cresyl Oxide [*o*-Tolyl Ether] and *o*-Cresylene Oxide [Di-*o*-tolylene Oxide]. ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 241—243. Compare this vol., i, 173).—On nitrating *o*-tolyl ether in acetic acid solution, a viscous liquid is obtained which, by distillation under reduced pressure, yields 5-*nitro*-o-*tolyl ether*, $C_6H_4Me\cdot O\cdot C_6H_3Me\cdot NO_2$, yellow needles, m. p. 125°; this on reduction with iron and acetic acid gives the corresponding *amine*, m. p. 98°. If the nitration is effected in cold fuming nitric acid, by gradual addition of the ether to the acid, 5 : 5′-*dinitro*-o-*tolyl ether*, $O(C_6H_3Me\cdot NO_2)_2$, is obtained as a white powder, m. p. 270°, which on prolonged nitration with fuming nitric acid, containing a little sulphuric acid, is converted into 3 : 5 : 3′ : 5′-*tetranitro*-o-*tolyl ether*,

$$O[C_6H_2Me\cdot(NO_2)]_2,$$

m. p. 115°.

Di-*o*-tolylene oxide nitrates very readily in acetic acid solution on warming, giving *nitrodi*-o-*tolylene oxide* $O<\begin{matrix}C_6H_3Me \\ | \\ C_6H_2Me\cdot NO_2\end{matrix}$, m. p. 108—109°, giving by reduction the corresponding *amine*, m. p. 92°, which gives a red coloration in alcoholic solution with calcium chloride.

By warming di-*o*-tolylene oxide with fuming nitric acid, a *dinitro*-derivative is obtained, crystallising in yellow needles, m. p. 170°. By warming this compound with fuming nitric acid, *tetranitrodi*-o-*tolylene oxide*, $O<\begin{matrix}CHMe(NO_2)_2 \\ | \\ C_6HMe(NO_2)_2\end{matrix}$, is obtained as a white powder, m. p. 210°. W. G.

The Action of Aldehydes on Phenols. HERMANN WICHELHAUS (*Ber.*, 1913, **46**, 110—112).—A continuation of research as to the origin of the dyes in certain woods (compare A., 1910, i, 868).

Formaldehyde has been detected in certain trees (Curtius and Franzen, A., 1912, ii, 978; Kleinstück, A., 1912, ii, 1202), and the author has, therefore, examined the action on phenols of trithioformaldehyde, which possesses the advantage of a lower volatility. In the presence of zinc chloride, condensation occurs with β-naphthol, resor-

cinol, α- and β-anthrols, and dihydroxynaphthalene, producing deeply coloured fusions which are difficult to purify. It is probable that one molecule, CH_2S, condenses with two of the phenol.

If the aldehyde is first combined with sodium sulphite (D.R.-P. 87335), the condensation follows another course, involving two molecules of aldehyde and two of the phenol; the products are colloidal substances often yielding fluorescent solutions, and possess dyeing power.

β-Naphthol after conversion into the acid, $OH\cdot C_{10}H_6\cdot CH_2\cdot SO_3H$, gives a condensation product which in solution possesses a green fluorescence, dyes wool a rose colour, and gives brightly coloured lakes with aluminium, manganese, and zinc salts. The product from β-naphtholsulphonic acid dyes silk greyish-red.

2 : 7-Dihydroxynaphthalene when converted into 2 : 7-dihydroxynaphthylmethanesulphonic acid, and heated slowly with zinc chloride solution in a vacuum, undergoes condensation below 100°, giving a blue *substance*, $C_{22}H_{16}O_6$; this dyes silk, and also can be converted into *nitro*-derivatives which also possess dyeing properties.

D. F. T.

The Silver Equivalent of Quinol. M. A. GORDON (*J. Physical Chem.*, 1913, **17**, 47—82).—The number of molecules of silver salt reduced per molecule of quinol varies with the conditions up to at least 10·5. In presence of acid no reduction occurs. In alkaline solution the amount of silver liberated from precipitated silver bromide depends on the efficiency of stirring, the time, temperature, and concentration of the alkali, but not on the incident light. At 20° in presence of excess of sodium hydroxide, the action appears to proceed in two stages, namely, up to about 6 equivalents of silver in a few hours, and then to about 8 in eighteen days. At 100° at least 9 equivalents are liberated in six hours.

The silver equivalent of *p*-benzoquinone is about two less than that of quinol. The liberation of 6 equivalents of silver by quinol corresponds with the formation of dihydroxy-*p*-benzoquinone, thus: $C_6H_4(OK)_2 + 6AgBr + 6KOH = C_6H_2(OK)_2O_2 + 6Ag + 6KBr + 4H_2O$. *p*-Benzoquinone and monohydroxy-*p*-benzoquinone may be intermediate products as suggested by Luther and Leubner (*Brit. J. Photo.*, 1912, **59**, 632—747), although the presence of neither monohydroxy- nor dihydroxy-benzoquinone has been demonstrated. *p*-Benzoquinone is undoubtedly an intermediate product, and by the action of the alkaline solution is transformed into quinol plus a peroxidised product which may be hydrogen peroxide (Mees and Sheppard) or hydroxybenzoquinone (Luther and Leubner). The Mees and Sheppard theory demands an infinite liberation of silver by a small amount of quinol in presence of sodium sulphite, and is inadmissible. The Luther and Leubner theory restricts the silver equivalent of quinol to 6, and therefore does not express the whole truth.

In strongly alkaline solution an excess of sodium sulphite increases the silver equivalent of quinol by 2 (from 6 to 8) for short runs, and by 1 (from 8 to 9) for long runs. The effect on the equivalent of benzoquinone is about half as great. When sulphite is added after the reduction by quinol has started, its effect is restricted. Hence

sulphite probably intervenes in the first and second stages of the oxidation of quinol equally. Some of the sulphite is oxidised, presumably to dithionate, although sodium sulphite alone is without action on silver bromide.

Ammoniacal silver nitrate, silver sulphite dissolved in sodium sulphite, and silver oxide in presence of sodium hydroxide give quinol equivalents of 7, 8, and 10·5 respectively for five minute runs.

Pyrogallol with and without sodium sulphite has a silver equivalent of a little over 3 when tested with silver bromide in a one hour run. Catechol under like conditions has an equivalent of 4·5, increasing to 5·5 in presence of sulphite. R. J. C.

o-Nitrophenyl Selenocyanate and o-Aminophenylselenol. HUGO BAUER (*Ber.*, 1913, **46**, 92—98).—When a solution of potassium selenocyanate is added gradually to a diazotised solution of o-nitroaniline in which the excess of free mineral acid has been neutralised by the addition of sodium acetate, nitrogen is liberated and a quantitative yield of o-*nitrophenyl selenocyanate*, yellow needles, m. p. 142°, is obtained. This action appears to be a general one, and was also successful with *p*-nitroaniline (p-*nitrophenyl selenocyanate*, pale yellow leaflets, m. p. 135°), sulphanilic acid, *p*-aminobenzoic acid, and arsanilic acid. On moistening with alcohol and then adding sodium hydroxide solution, *o*- and *p*-nitrophenyl selenocyanates undergo hydrolysis, forming coloured solutions (violet and red respectively) of the *sodium* salts of o- and p-*nitrophenylselenols*; the free phenylselenols could not be isolated, but the addition of a solution of lead acetate precipitated the *lead* salts, both of an orange colour.

The coloured alkaline solution of *o*-nitrophenylselenol soon loses its colour, undergoing oxidation even in a hydrogen atmosphere to *di*-o-*nitrophenyl diselenide*, yellow needles, m. p. 209°, which precipitates. The alkaline solution of *o*-nitrophenylselenol can also be obtained by the interaction of *o*-chloronitrobenzene and sodium hydroselenide in dilute solution in cold alcohol, and the diselenide can then be again obtained, the oxidation being aided if necessary by the addition of hydrogen peroxide. The former method is, however, the more satisfactory.

If the alkaline solution of *o*-nitrophenylselenol is treated near its b. p. with sodium hyposulphite a clear yellow or colourless solution of the *sodium* salt of o-*aminophenylselenol* is obtained, which on careful oxidation with hydrogen peroxide gives a precipitate of *di*-o-*aminophenyl diselenide*, orange needles, m. p. 81°. When a solution of this in hot alcohol is treated with hydrochloric acid and the resultant suspension of the *hydrochloride* reduced by zinc dust, the addition of sodium acetate precipitates the stable *zinc* salt of *o*-aminophenylselenol; the action of lead acetate on a suspension of this gives the orange *lead* salt. The reduction of the diselenide can also be effected by alkali and dextrose (compare Clasz, A., 1912, i, 851).

The action of benzoyl chloride on the zinc salt of *o*-aminophenylselenol in the presence of ethyl acetate produces 1-*phenylbenzoselenazole*, $C_6H_4<^{N}_{Se}>CPh$, colourless needles, m. p. 116—117° which could not

be obtained by the action of selenium on benzanilide (compare Hofmann, A., 1880, 386; 1887, 839). With picryl chloride the zinc salt undergoes condensation with the formation of 3:5-*dinitrophenoselenazine*, $C_6H_4<\substack{NH \\ Se}>C_6H_2(NO_2)_2$ (compare Kehrmann, A., 1900, i, 61).

D. F. T.

Some Compounds of Cholesterol giving Liquid Crystals. Paul Gaubert (*Compt. rend.*, 1913, **156**, 149—151. Compare A., 1907, ii, 932; 1908, i, 882; 1909, i, 920).—On heating cholesterol with the different tartaric acids for one minute a homogeneous isotropic liquid substance is obtained, which on cooling yields elongated rhombic crystals, possessing very great plasticity. The direction of the greatest refraction coincides with the long diagonal. At temperatures near to the point of fusion, the crystalline particles of the crystals arrange themselves so that the optical axis is perpendicular to the glass slide, and there are produced extensive, irregular films exhibiting all the characteristics of a uniaxial, optically positive substance. The hardness of the crystals rapidly increases up to that of gypsum as they become solid. Similar results are obtained by using malic and lactic acids instead of the tartaric acids. Maleic and malonic acids, but not fumaric acid, yield optically positive liquid crystals almost instantly on warming with cholesterol, but they are only stable within narrow temperature limits. The same applies to the compound obtained with succinimide and cholesterol. In order to obtain liquid crystals with cholesterol and succinic, cinnamic, or anisic acids, it is necessary to keep the mixture molten at 160° for one hour, when characteristic optically negative crystals are produced.

W. G.

Action of Magnesium on a Mixture of Allyl Bromide and Benzoin. V. Jakubovitsch (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1858—1861).—*Diphenylallylethylene glycol* [*δε-diphenyl-Δ^α-pentene-δε-diol*], $C_3H_5\cdot CPh(OH)\cdot CHPh\cdot OH$, prepared by decomposing with water the product of the action of magnesium on allyl bromide and benzoin, forms small, colourless crystals, m. p. 89°, has the normal molecular weight in boiling benzene, and decolorises bromine. When boiled with 20% sulphuric acid, it is converted into the corresponding double *ether*, $\begin{matrix} CHPh—O—CHPh \\ | \qquad\qquad | \\ CPh(C_3H_5)\cdot O\cdot CPh\cdot C_3H_5 \end{matrix}$, which crystallises in small, colourless needles, m. p. 125—126°.

T. H. P.

Influence of Constitution on the Rotatory Power of Optically Active Substances. V. Esters of *d*-Carvoxime. Hans Rupe and Georg Wolfsleben (*Annalen*, 1913, **395**, 136—148).—The following substances have been prepared generally by the interaction of *d*-carvoxime, pyridine (2 mols.), and the acyl chloride in benzene. Only the acetyl compound can be purified by distillation under diminished pressure; the others must be crystallised from absolute or dilute alcohol. Acetylcarvoxime has m. p. 63—64°, b. p. 158—161°/17 mm., and $[\alpha]_D^{20}$ +43·02°. *Crotonylcarvoxime*, $C_{10}H_{14}:NO\cdot CO\cdot CH:CHMe$, oil,

$[\alpha]_D^{20}$ $+33{\cdot}46°$; *diphenylacetylcarvoxime*, m. p. 65—66°, $[\alpha]_D^{20}$ $+17{\cdot}63°$; *cinnamoylcarvoxime*, m. p. 79°, $[\alpha]_D^{20}$ $+15{\cdot}44°$; *β-phenylpropionylcarvoxime*, oil, $[\alpha]_D^{20}$ $+26{\cdot}23°$; *α-phenylcinnamoylcarvoxime*,

$C_{10}H_{14}$:N·O·CO·CPh:CHPh,

m. p. 139—140°, $[\alpha]_D^{20}$ $+37{\cdot}06°$; *αβ-diphenylpropionylcarvoxime*, m. p. 119—120°, $[\alpha]_D^{20}$ $+12{\cdot}52°$; *β-phenylcinnamoylcarvoxime*, m. p. 74—75°, $[\alpha]_D^{20}$ $+26{\cdot}37°$; *di-β-phenylpropionylcarvoxime*, m. p. 89—90°, $[\alpha]_D^{20}$ $+20{\cdot}09°$; *α-methylcinnamoylcarvoxime*, m. p. 68—69°, $[\alpha]_D^{20}$ $+16{\cdot}33°$; *β-phenyl-α-methylpropionylcarvoxime*, oil, $[\alpha]_D^{20}$ $+23{\cdot}85°$; *β-methylcinnamoylcarvoxime*, m. p. 78°, $[\alpha]_D^{20}$ $+22{\cdot}45°$; *β-phenyl-β-methylpropionylcarvoxime*, oil, $[\alpha]_D^{20}$ $+22{\cdot}76°$.

Excluding the α- and the β-phenylcinnamoyl- and diphenylpropionylcarvoximes, the rotation of the saturated or the alkyl derivatives is distinctly greater than that of the corresponding unsaturated or phenyl derivatives. A parallelism cannot be traced between the carvoxime esters and the menthyl esters of the acids.

The entrance of a phenyl group into acetic acid or phenylacetic acid or the replacement of methyl by phenyl in acetic acid or crotonic acid diminishes the rotatory power of the carvoxime; the entrance of phenyl into the α- or the β-position in cinnamic acid increases the rotatory power. Just the converse behaviour is observed with the menthyl esters of the acids. The author is of opinion that the work so far recorded proves the necessity of dealing with substances containing one, or at most two, asymmetric carbon atoms in connexion with the problem of the relation between constitution and rotatory power. C. S.

The Determination of the Configuration of the Stereoisomeric Cinnamic Acids. Carl Liebermann (*Ber.*, 1913, **46**, 214—216).—A reply to Stoermer and Heymann (A., 1912, i, 974), indicating that theirs is not the first experimental proof of the steric configuration of *allo*cinnamic acid. D. F. T.

Fixation of the Alkali Hydrogen Sulphites by the Salts and Esters of the Acetylenic Acids. Ed. Lasausse (*Compt. rend.*, 1913, **156**, 147—149).—Under given conditions the salts or esters of the acetylenic acids of the type R·C:C·CO_2H will unite with one or two molecules of an alkali hydrogen sulphite, giving an alkali salt of a monosulphonic acid, containing an ethylenic linking, or of a saturated disulphonic acid.

On heating phenylpropiolic acid (1 mol.) with normal sodium sulphite (1·5 mol.) in aqueous solution, in a sealed tube for eight hours at 100°, crystals of *disodium-β-sulphocinnamate*,

SO_3Na·CPh:CH·CO_2Na,

are obtained, which rapidly decolorise potassium permanganate in the cold. When heated in sealed tubes at 130° with concentrated hydrochloric acid it is decomposed, giving carbon dioxide, sulphur dioxide, and acetophenone. On fusion with sodium hydroxide at 200—220°, it yields sodium benzoate, sodium acetate, and sodium sulphite. The corresponding *potassium* salt has been prepared, starting with potassium sulphite. Methyl phenylpropiolate and sodium hydrogen sulphite under similar conditions yield *sodium methyl sulphocinnamate*,

SO_3Na·CPh:CH·CO_2Me.

If the heating is carried on for forty hours under reflux instead of in sealed tubes, three compounds are obtained, namely, *methyl disodium disulphophenylpropionate*, $C_2H_2Ph(SO_3Na)_2\cdot CO_2Me$, disodium sulphocinnamate, and *sodium phenyldisulphopropionate*,

$$C_2H_2Ph(SO_3Na)_2\cdot CO_2Na.$$

These three substances can be separated by their varying solubility in alcohol. The *barium* salt corresponding with the last compound has been prepared.

By similar methods the author has prepared *methyl disodium disulpho-octoate*, $C_5H_{11}\cdot C_2H_2(SO_3Na)_2\cdot CO_2Me$, which is saponified by cold aqueous sodium hydroxide, giving the corresponding *trisodium* salt, which when heated with hydrochloric acid in sealed tubes at 120° yields the *acid*, $C_5H_{11}\cdot C_2H_2(SO_3Na)_2\cdot CO_2H$.

He also prepared *methyl disodium disulphononoate*,

$$C_6H_{13}\cdot C_2H_2(SO_3Na)_2\cdot CO_2Me,$$

the *trisodium* derivative, and the *acid*, $C_6H_{13}\cdot C_2H_2(SO_3Na)_2\cdot CO_2H$.

W. G.

Synthesis of β-m-Tolyl-α-methylhydracrylic Acid. A. GUBAREV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1865—1867).—*Ethyl β-m-tolyl-α-methylhydracrylate*, $C_6H_4Me\cdot CH(OH)\cdot CHMe\cdot CO_2Et$, obtained by decomposing with water the product of the action of zinc on a mixture of ethyl α-bromopropionate and *o*-tolualdehyde, is a colourless, viscous liquid, with a pleasant odour, b. p. 171—172°/15—16 mm. The *acid* forms crystals, m. p. about 90°, but was not obtained pure. The *potassium* $(+H_2O)$, *silver*, *zinc*, *copper*, and *lead* salts were prepared, and the first two analysed.

T. H. P.

Influence of Constitution on the Rotatory Power of Optically Active Substances. IV. HANS RUPE (*Annalen*, 1912, **395**, 87—135).—[With EDUARD LENZINGER.]—The following menthyl esters have been prepared by heating menthol and the substituted ethyl acetoacetate; acetoacetate, m. p. 36°, b. p. 154°/10 mm.; *methylacetoacetate*, $CH_3\cdot CO\cdot CHMe\cdot CO_2\cdot C_{10}H_{19}$, b. p. 148—149°/8 mm., $[\alpha]_D^{20}$ $-63.59°$ in benzene, n_α 1·45436, n_D 1·45733, n_β 1·46317, n_γ 1·46797, D_4^{20} 0·9697, violet coloration with alcoholic ferric chloride; ethylacetoacetate, b. p. 155°/8 mm., $[\alpha]_D^{20}$ $-60.26°$ in benzene, violet coloration with ferric chloride. The following menthyl esters are prepared by heating menthyl sodioacetoacetate and the requisite alkyl haloid in ethyl alcohol: *propylacetoacetate*, b. p. 162°/8 mm., $[\alpha]_D^{20}$ $-57.27°$ in benzene, reddish-violet coloration with alcoholic ferric chloride; sec.-*octylacetoacetate*, b. p. 139°/0·1 mm., $[\alpha]_D^{20}$ $-47.82°$ in benzene, brownish-red coloration with ferric chloride. *Menthyl phenylacetoacetate*, prepared from menthol and ethyl phenylacetoacetate at 140°, has m. p. 69°, b. p. 131—133°/0·1 mm., and develops a violet coloration with alcoholic ferric chloride. A freshly prepared solution of the ester in benzene is dextrorotatory, $[\alpha]_D^{20}$ $+19.07°$, but rapidly becomes lævorotatory, and has $[\alpha]_D^{20}$ $-67.55°$ constant after ten days. In another experiment, $[\alpha]_D^{20}$ was initially $+28.70°$, and finally constant at $-67.16°$ after sixty-seven days. In alcohol, $[\alpha]_D^{20}$ is initially $-28.27°$, and becomes constant at $-67.15°$ after forty-seven hours.

Menthyl benzylacetoacetate, prepared from menthol and ethyl benzylacetoacetate at 155°, has m. p. 68°, and $[\alpha]_D^{20}$ −106·97°, and produces with alcoholic ferric chloride a yellow coloration changing to greyish-yellow. By treatment with benzyl bromide and alcoholic sodium ethoxide at 0°, it yields *menthyl dibenzylacetoacetate*, m. p. 70°, $[\alpha]_D^{20}$ −25·28°.

Menthyl sodioacetoacetate and the requisite haloid in alcohol yield the following menthyl esters: *β-phenylethylacetoacetate*,

$$CH_2Ph\cdot CH_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19},$$

b. p. 143°/0·1 mm., $[\alpha]_D^{20}$ −51·64° in benzene and −53·79° in alcohol, violet coloration with ferric chloride; *γ-phenylpropylacetoacetate*, b. p. 157°/0·1 mm., $[\alpha]_D^{20}$ −45·44° in benzene and −48·99° in alcohol; *allylacetoacetate*, b. p. 169—171°/13 mm., $[\alpha]_D^{20}$ −58·27° in benzene; *cinnamylacetoacetate*, $CHPh{:}CH\cdot CH_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19}$, $[\alpha]_D^{20}$ −41·31° in benzene.

Menthyl benzoylacetate, $CH_2Bz\cdot CO_2\cdot C_{10}H_{19}$, prepared from ethyl benzoylacetate and menthol at 120°, has m. p. 41°, $[\alpha]_D^{20}$ n benzene initially −55·36° and finally −63·97° after fifty hours, $[\alpha]_D^{20}$ in alcohol initially −56·41° and finally −56·89° after six hours, is slightly soluble in alkalis, develops a deep red coloration with alcoholic ferric chloride, and forms a *semicarbazone*, m. p. 163°, which produces a dark green coloration with ferric chloride.

The following menthyl esters are obtained by treating menthyl sodiobenzoylacetate with the requisite alkyl haloid in alcohol; *α-benzoylpropionate*, $CHMeBz\cdot CO_2\cdot C_{10}H_{19}$, m. p. 68°, $[\alpha]_D^{20}$ −57·73° in alcohol; *α-benzoylbutyrate*, b. p. 208°/10 mm., $[\alpha]_D^{20}$ −55·86° in alcohol and −54·27° in benzene; *α-benzoylvalerate*, decomp. 180°/0 mm., $[\alpha]_D^{20}$ −52·35° in alcohol, violet-red coloration with alcoholic ferric chloride.

Ethyl benzoylphenylacetate and menthol at 160—165° yield *menthyl benzoylphenylacetate*, m. p. 116°, $[\alpha]_D^{20}$ +20·14° in benzene and −12·12° initially and −62·60° after eighty-nine hours in alcohol.

The following menthyl esters are obtained from menthyl sodiobenzoylacetate and the requisite haloid in alcohol: *α-benzoyl-β-phenylpropionate*, m. p. 117°, $[\alpha]_D^{20}$ −60·83° in benzene; *α-benzoyl-γ-phenylbutyrate*, m. p. 77°, $[\alpha]_D^{20}$ −56·70° in benzene; *α-benzoyl-δ-phenylvalerate*, $[\alpha]_D^{20}$ −43·97°; *α-benzoyl-Δ^γ-pentenoate*, m. p. 53°, $[\alpha]_D^{20}$ −51·40° in benzene, violet-red coloration with ferric chloride in alcohol; *α-benzoyl-δ-phenyl-Δ^γ-pentenoate*, m. p. 82—83°, $[\alpha]_D^{20}$ −48·10°.

By esterifying α-benzoyl-δ-phenyl-Δ^γ-pentenoic acid with menthol and repeatedly extracting the product with gasolin, it can be resolved in the sparingly soluble l-*menthyl* l-*α-benzoyl-δ-phenyl-Δ^γ-pentenoate*, m. p. 102—103°, $[\alpha]_D^{20}$ −86·66° in benzene, colourless needles, and the more soluble l-*menthyl* d-*α-benzoyl-δ-phenyl-Δ^γ-pentenoate*, m. p. 77°, $[\alpha]_D^{20}$ −25·95° in benzene; the esters do not develop a coloration with alcoholic ferric chloride.

Menthyl benzoylacetate and benzaldehyde and a little piperidine, cooled in a freezing mixture, yield *menthyl α-benzoylcinnamate*, $CHPh{:}CBz\cdot CO_2\cdot C_{10}H_{19}$, m. p. 65°, $[\alpha]_D^{20}$ −77·43° in benzene white leaflets.

[With PAUL HÄUSSLER.]—α-Benzylcinnamoyl chloride and mentho

in benzene containing pyridine yield *menthyl a-benzylcinnamate*,

$$CHPh\colon C(CH_2Ph)\cdot CO_2\cdot C_{10}H_{19},$$

m. p. 64—65°, $[\alpha]_D^{20} -144\cdot 86°$ in benzene, and *a-benzylcinnamic anhydride*, $O[CO\cdot C(CH_2Ph)\colon CHPh]_2$, m. p. 108—109°. The latter, which is stable to boiling aqueous sodium carbonate and is only slowly esterified by boiling alcohol and sulphuric acid, is also obtained directly from the acid chloride and pyridine.

Menthyl β-phenyl-a-benzylpropionate, m. p. 42—43°, $[\alpha]_D^{20} -24\cdot 41°$ in benzene, is prepared from the acid chloride, menthol, and pyridine in benzene.

[With GEORG WOLFSLEBEN.]—The reaction between potassium γ-phenylbutyrate and an excess of benzaldehyde and of acetic anhydride at 106° for forty-eight hours, and subsequently on the water-bath for 290 hours, leads to the formation of *γ-phenyl-a-benzylidenebutyric acid*, $CH_2Ph\cdot CH_2\cdot C(\colon CHPh)\cdot CO_2H$, m. p. 124—125°. Its *menthyl* ester, prepared from the acid chloride, menthol, and pyridine in benzene, is a yellow oil, $[\alpha]_D^{20} -23\cdot 00°$.

Ethyl sodiomalonate and β-phenylethyl bromide in boiling alcohol yield *ethyl β-phenylethylmalonate*, $CH_2Ph\cdot CH_2\cdot CH(CO_2Et)_2$, b. p. 179°/10 mm., which reacts with alcoholic sodium ethoxide and benzyl bromide to form *ethyl benzyl-β-phenylethylmalonate*,

$$CH_2Ph\cdot CH_2\cdot C(CH_2Ph)(CO_2Et)_2,$$

b. p. 230°/10 mm. By hydrolysis with methyl alcoholic potassium hydroxide, the latter yields *benzyl-β-phenylethylmalonic acid*, m. p. 153° (decomp.), which is converted at 160° into *γ-phenyl-a-benzylbutyric acid*, $CH_2Ph\cdot CH_2\cdot CH(CH_2Ph)\cdot CO_2H$, m. p. 59—61°, b. p. 230°/8 mm. The acid chloride of the latter yields the *menthyl* ester, m. p. 102°, $[\alpha]_D^{20} -36\cdot 69°$, by treatment with menthol and pyridine in benzene, and is converted by distillation under 15 mm. partly into *2-β-phenylethylhydrindone*, $C_6H_4<\begin{matrix}CO\\CH_2\end{matrix}>CH\cdot CH_2\cdot CH_2Ph$, m. p. 56—57° (*semicarbazone*, m. p. 227—228° [decomp.]). γ-Phenylpropyl bromide and potassium cyanide yield *γ-phenylbutyronitrile*, b. p. 132—133°/11 mm. The acid is converted by phosphorus trichloride in benzene into the *chloride*, b. p. 119°/9 mm., from which *menthyl γ-phenylbutyrate*, b. p. 205°/10 mm., $[\alpha]_D^{20} -57\cdot 00°$, is obtained by means of menthol and pyridine in benzene.

The variations with time of the rotations of the preceding menthyl esters of β-ketonic acids in alcohol and in benzene have been measured in order to gain some idea of the magnitude and the velocity of the keto-enolic transformation. The acetoacetate and benzoylacetate rapidly acquire a constant rotation in a alcohol, but only after many hours or even days in benzene; the methylacetoacetate, benzoylpropionate, and benzoylphenylpropionate have constant rotations in benzene as well as in alcohol.

An unexpected fact of great importance has been found in the resolution by crystallisation of the menthyl esters of β-ketonic acids of enantiomorphous configuration. Such esters, the phenylacetoacetate, benzylacetoacetate, benzoylphenylacetate, and benzoylphenylpentenoate, all of which, it will be observed, contain a phenyl group, must have the ketonic structure. The case of the menthyl phenyl-

acetoacetate is interesting. Only *l*-menthyl *d*-phenylacetoacetate has been isolated, and it is dextrorotatory. As it changes to the enol in benzene, the activity due to the acidic portion disappears, the activity finally being due to the *l*-menthyl group only; the time required for the attainment of a constant lævorotation varies in different experiments (probably owing to the action of a catalyst in the glass), in one case being ten days and in another sixty-five days. The converse is observed with *l*-menthyl *d*-benzoylphenylacetate, which has a constant dextrorotation in benzene, but is lævorotatory in alcohol, reaching a maximum after four days.

Menthyl benzyl-, dibenzyl-, and benzylidene-acetoacetates, and the methyl-, phenyl-, benzyl-, *s*-phenylethyl-, cinnamyl-, and benzylidene-derivatives of menthyl benzoylacetate do not develop a coloration with alcoholic ferric chloride. In some cases the enolisation must be repressed by the ferric chloride, because menthyl benzoylphenylacetate, for example, which does not give a coloration with alcoholic ferric chloride, shows in alcohol a lævorotation which increases with time.

The author's results show that valuable conclusions regarding structure can be drawn from the molecular rotations, provided strictly homologous esters are being compared; comparisons are not justifiable when an alkyl group is replaced by a phenyl group. C. S.

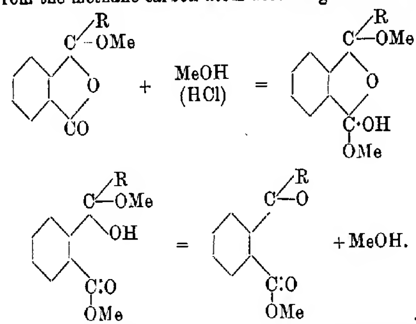
α-Hydroxy-γ-phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate. J. BOUGAULT (*Compt. rend.*, 1913, 156, 236—239. Compare A., 1912, i, 770, and Fittig, A., 1898, i, 196).—By the controlled action of dilute sodium hydroxide on α-hydroxy-γ-phenylcrotonamide, and subsequent neutralisation with acid, an *acid amide* is obtained having the constitution

$$\begin{array}{l} CH_2Ph\cdot CH_2\cdot C(OH)\cdot CO_2H \\ \qquad\qquad\quad >O \\ CH_2Ph\cdot CH_2\cdot C(OH)\cdot CO\cdot NH_2 \end{array},$$

which on heating loses two molecules of water, giving another *acid amide*, $C_{20}H_{19}O_4N$. The first compound is readily decomposed by alkalis or alkali carbonates quantitatively into ammonia and benzylpyruvic acid, but unlike the acid anhydrides is not hydrated by boiling with water or dilute acetic acid. W. G.

Esters of Aromatic Keto-acids. GRETE EGERER and HANS MEYER (*Monatsh.*, 1913, **34**, 69—93. Compare A., 1908, i, 26).—The pseudo- and normal esters of some benzoylated benzoic acids are described. In most cases the ψ-methyl esters, for which the sensitive colour reaction with concentrated sulphuric acid is characteristic, are produced by the action of thionyl chloride, but Goldschmiedt and Lipschitz had already shown (A., 1905, i, 132) that the *n*-ester resulted in the case of naphthoylbenzoic acid, whilst ψ-ethyl esters were hitherto unknown. It is now demonstrated that the ψ-ester is the primary product in all cases, but that under the influence of alcohol and mineral acids it may undergo further changes which result in the *n*-ester. To prevent this rearrangement, for example, in the case of the naphthoylbenzoate, the mixture of the acid chloride and the alcohol is immediately poured into sodium carbonate solution. On the other hand, any ψ-ester may be converted into its isomeride by the action of

a mineral acid or thionyl chloride and an alcohol. In this way a ψ-methyl ester may be transformed into a n-ethyl ester, which might be supposed to be due to the effect of mass action on the already rearranged n-methyl ester. Since, however, prolonged heating with methyl alcohol is necessary to convert ethyl n-benzoylbenzoate into the n-methyl ester, whereas the ψ-ethyl ester gives the n-methyl ester in a short time, the conclusion is drawn that the transformation of the ψ-form into the n-form is not due to any instability of the chloride or of the ester, but to the addition of alcohol to the lactone system under the catalytic influence of hydrogen ions and the subsequent elimination of alcohol from the methane carbon atom according to the scheme:



It thus becomes evident why the action of ammonia on the isomerides always results in the same amide, namely, that of the ketone acid (compare Meyer, A., 1905, i, 133).

Some of the acids employed were derived from the chlorophthalic acid which Auerbach obtained by the action of hypochlorites on phthalic acid. Since this may be condensed with benzene and transformed into β-chloroanthraquinone, it is to be regarded as 4-chlorophthalic acid.

Whereas methyl ψ-benzoylbenzoate may be prepared without precaution, by the action of thionyl chloride and methyl alcohol, the formation of the *ψ-ethyl* ester only succeeds when the mixture of the chloride with excess of cold absolute alcohol is at once poured into cold sodium carbonate solution. It crystallises in triangular tablets, m. p. 51—53°, and dissolves with lemon-yellow colour in concentrated sulphuric acid. The n-ethyl ester (rhombic, $a:b:c = 1\cdot9725:1:1\cdot267$) may be prepared by leaving the chloride with alcohol, by the usual means or by boiling the ψ-methyl ester for a few minutes or the n-methyl ester for a few hours with alcohol and thionyl chloride or sulphuric acid. Conversely, methyl alcohol and thionyl chloride transform the ψ-ethyl ester into the n-methyl ester in a short time, whereas the n-ethyl ester must be heated for fifty hours. In the same way, methyl ψ-toluoylbenzoate and methyl ψ-methoxybenzoylbenzoate (Meyer and Turnau, A., 1909, i, 710; m. p. 83° and not 63°) may be converted into the n-esters.

The preparation of 4-chlorophthalic anhydride by Auerbach's

method has been improved; the compound has b. p. 291—295°, and when crystallised from dry ether has m. p. 94°, but after contact with moist ether the m. p. rises to that of the acid. When condensed with benzene in presence of an excess of aluminium chloride, it yields *benzoyl-4-chlorobenzoic acid*, m. p. 180·5°, which gives β-chloroanthraquinone (Graebe and Rée, T., 1886, 531) in concentrated sulphuric acid. The *acid chloride*, $COPh{\cdot}C_6H_3Cl{\cdot}COCl$, long needles, m. p. 114—117°, also readily yields the quinone on heating. The *ψ-methyl ester* forms colourless needles, m. p. 68·5—69·5°, and the n-*ester* forms monoclinic crystals ($a:b:c=1{\cdot}8252:1:0{\cdot}6878$; $\beta=76°59'$), m. p. 102—104°.

The acid obtained by the condensation of 4-chlorophthalic anhydride with chlorobenzene dissolves in sulphuric acid with the formation of 2:6-dichloroanthraquinone, and is, therefore, 2-p-*chlorobenzoyl-4-chlorobenzoic acid*, which confirms the position of the halogen in the above benzoyl-4-chlorobenzoic acid. The acid has m. p. 195·5°, gives a well-defined *acid chloride*, m. p. 115—120°, from which, however, the ψ-ester could not be obtained crystalline. The n-*methyl* ester, from the transformation of the crude isomeride or by direct esterification, melts at 98°.

Methyl ψ-p-*chlorobenzoylbenzoate*, m. p. 101—102·5°; the n-*ester*, m. p. 109—110°, monoclinic crystals ($a:b:c=0{\cdot}92461:1:?$; $\beta=73°40'$), and the n-*ethyl* ester, m. p. 88°, have also been prepared.

Phthalic anhydride condenses with *p*-dichlorobenzene when boiled with an excess of aluminium chloride in nitrobenzene; the 2-om-*dichlorobenzoylbenzoic acid*, radiating needles, m. p. 168°, yields 1:4-dichloroanthraquinone (Ullmann and Billig, A., 1911, i, 490). Similarly, 4-chlorophthalic anhydride and *p*-dichlorobenzene give 2-om-*dichlorobenzoyl-4-chlorobenzoic acid*, m. p. 157—160°, which condenses to form 1:4:7-trichloroanthraquinone and yields a *ψ-methyl* ester, m. p. 115—120°.

The constitution of the isomeric esters (A., 1908, i, 26) receives support from the molecular refractions, for methyl *n*-benzoylbenzoate, $[M.R.]_D=67{\cdot}98$, being a benzophenone derivative, shows exaltation (compare Auwers and Eisenlohr, A., 1911, ii, 782), whereas the ψ-ester gives the theoretical value for a hydroxylactone, $[M.R.]_D=65{\cdot}40$.

J. C. W.

Isomeric Esters of Trichlorobenzoylbenzoic Acids. STEPHAN JAROSCHY (*Monatsh.*, 1913, **34**, 1—6. Compare preceding abstract). —The product of the condensation of 1:4-dichlorophthalic anhydride with chlorobenzene, 2-p-*chlorobenzoyl*-3:6-*dichlorobenzoic acid*,

$$C_{14}H_7O_3Cl_3,$$

crystallises in colourless leaflets, m. p. 157°, and yields 1:4:7-trichloroanthraquinone in concentrated sulphuric acid. The *ψ-methyl* ester, colourless crystals, m. p. 153—154°, and the *ψ-ethyl* ester, a white, crystalline powder, m. p. 150—151°, may be obtained by immediately adding the mixture of alcohol and acid chloride to sodium carbonate solution, and may be transformed into the *n*-esters by heating with thionyl chloride and the corresponding alcohol for some hours. The normal esters may also be obtained by the usual methods, give no

coloration in sulphuric acid, and melt at 90° and 105—106° respectively. J. C. W.

Preparation of Amides and Acylation of the Amino-group. HERMAN DECKER (*Annalen*, 1913, **395**, 282—299).—Hofmann's classical method of preparing amides and substituted amides by heating the ammonium salts of carboxylic acids or their salts with primary and secondary amines, which has fallen into disuse owing to its supposed disadvantages, is shown to be a simple and convenient method of preparation provided the optimum temperature (the temperature at which water is eliminated, it may be slowly, from the salt, whilst the dissociation of the latter is still hardly appreciable) is obtained, and is retained to the end of the reaction. A whole series of amides and substituted amides have thus been prepared by simply heating the acid and the amine at the optimum temperature. The reaction, which is analogous to the formation of an ester from an acid and an alcohol, is accelerated, as in the case of esterification, by catalysts.

[With WALTER KROPP, HEINRICH HOYER, CLEMENS ZOELLNER, and PAUL BECKER.]—Formophenylethylamide is obtained free from β-phenylethylamine formate, and in 96% yield by heating β-phenylethylamine and anhydrous formic acid in slight excess at 170—180° for four hours. In a similar manner, phenylacetyl-β-phenylethylamine (95% yield) is obtained from phenylacetic acid and the amine at 180°, and acetyl-β-phenylethylamine from acetic acid and the amine.

Piperonylacetamide, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, m. p. 122—123°, colourless leaflets, can be prepared from the acid chloride and 25% aqueous ammonia, from *ethyl piperonylacetate*, b. p. 303°, and aqueous ammonia at 160—180° (bad yield), or from 3:4-methylenedioxyphenylpropionyl chloride and 25% aqueous ammonia, is readily obtained by heating piperonylacetic acid for two hours at 200—220° in a current of dry ammonia. It is readily converted by the sodium hypochlorite method into homopiperonylamine (hydrochloride, m. p. 207—208°; picrate, m. p. 174—176°; *carbonate*, m. p. about 110°; *platinichloride*, m. p. about 225° [decomp.]).

Formohomopiperonylamide, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CHO$, m. p. 61—62°, is obtained almost quantitatively from the amine and anhydrous formic acid at 180—200°. *Phenylacetohomopiperonylamide*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, m. p. 96°, is obtained from the amine and phenylacetic acid at 160°.

Homopiperonoylhomopiperonylamine,

$$CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3{:}CH_2O_2,$$

m. p. 119°, is prepared from the amine and homopiperonylic acid at 160° for eight hours. Homopiperonylic acid is obtained in 5% yield by oxidising safrole in well-cooled acetone with potassium permanganate and treating the precipitate with sulphurous acid, whereby piperonylic acid is precipitated; the homopiperonylic acid is extracted from the filtrate by ether.

Anhydrous oxalic acid reacts with β-phenylethylamine at 180—200° to form oxalodi-β-phenylethylamide, m. p. 186°, in 61% yield, and with homopiperonylamine at 170—180° to form *oxalodihomopiperonyl-*

amide, $C_2O_2(NH\cdot CH_2\cdot CH_2\cdot C_6H_3\text{:}CH_2O_2)_2$, m. p. 196—197° (corr.), colourless needles.

Fagaramide (Thoms and Thümen, A., 1912, i, 115) can be synthesised by heating piperonylacrylic acid and *iso*butylamine at 190—200° for two and a-half hours. C. S.

The Oxidation of Substituted Aceanthrenequinones. D. Butescu (*Ber.*, 1913, **46**, 212—214. Compare Liebermann and Butescu, A., 1912, i, 467).—The substituted aceanthrenequinones behave on oxidation in a similar manner to aceanthrenequinone itself, yielding anthraquinonecarboxylic acids (Liebermann and Zsuffa, A., 1911, i, 202). The oxidation is effected in acetic acid solution by chromic acid.

β-Methylanthraquinone-α-carboxylic acid, yellow needles, m. p. 295°, is obtained in the oxidation of β-methylaceanthrenequinone.

β-Chloroanthraquinone-α-carboxylic acid, yellow needles, m. p. 260°, obtained from β-chloroaceanthrenequinone, is distinct from the β-chloroanthraquinonecarboxylic acid described by Heller and Schülke (A., 1908, i, 994).

α-Chloroanthraquinone-α-carboxylic acid, obtained by the oxidation of α-chloroaceanthrenequinone, forms leaflets, m. p. 205°, which can be sublimed to give yellow needles; it is distinct from the isomeric substances described by Heller and Schülke (*loc. cit.*) and Fischer and Sapper (A., 1911, i, 279).

1 : 5-*Dichloroanthraquinone-4-carboxylic acid*, obtained from 1 : 5-dichloroaceanthrenequinone, has m. p. 250°.

1 : 8-*Dichloroanthraquinone-5-carboxylic acid*, from the corresponding aceanthrenequinone, forms yellow needles, m. p. 240°. D. F. T.

Action of Magnesium on a Mixture of Allyl Bromide and Phthalic Anhydride. A. Orlov (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1868—1870. Compare Bauer, Abstr., 1904, i, 417; 1905, i, 210).

Diallylphthalide, $C_6H_4{<}{\overset{C(C_3H_5)_2}{\underset{CO}{}}}{>}O$, prepared by the action of water on the product of the interaction of magnesium, allyl bromide, and phthalic anhydride, is a pale yellow, slightly mobile liquid of pleasant odour, b. p. 184—185°/14 mm., D_4^{25} 1·0546, n_D^{25} 1·53614, and develops fluorescence on prolonged keeping. It unites with 4 atoms of bromine, giving a liquid *bromide*, $C_{14}H_{14}O_2Br_4$, of pleasant odour. T. H. P.

The Reaction between 5-Bromo-2 : 4 : 6-tri-iodo-1 : 3-dinitrobenzene and Ethyl Sodiomalonate. C. Loring Jackson and F. C. Whitmore (*Ber.*, 1913, **46**, 67—70).—The explanation (Jackson and Bigelow, A., 1911, i, 101) of the reaction between ethyl sodiomalonate and halogen-nitrobenzenes in which one of the halogen atoms of the latter becomes replaced by hydrogen is now tested by applying it to 5-bromo-2 : 4 : 6-tri-iodo-1 : 3-dinitrobenzene; this substance is found, in accordance with the hypothesis, first to form with the ethyl sodiomalonate, an *additive* compound which probably has the constitution

$CO_2Et\cdot CHI\cdot C(ONa)(OEt)\cdot C_6BrI_2(NO_2)_2$, which when acidified undergoes scission into $C_6HBrI_2(NO_2)_2$ and $CHI(CO_2Et)_2$, the latter substance then reacting with a second molecule of ethyl sodiomalonate with the formation of ethyl ethanetetracarboxylate.

The additive compound could not be isolated, but a mixture of 2-bromo-1 : 3 : 5-tri-iodo-4 : 6-dinitrobenzene and ethyl sodiomalonate in alcohol gives a deep red liquid; if an excess of the halogen compound or of ethyl sodiomalonate is taken and a little of the filtered red liquid is evaporated, the percentages of sodium in the residue in the former case and of halogen in the latter are in accord with the above composition.

The direct coupling of the substituted benzene ring with the ethyl sodiomalonate is attributed to the possibility that the substituted ring is more negative than the iodine atom, and it is held that the formation of *p*-toluenesulphinic acid and ethyl ethanetetracarboxylate from *p*-toluenesulphonyl chloride and ethyl sodiomalonate (Kohler and MacDonald, A., 1899, i, 907) is in support of such a view.

D. F. T.

Polymerisation of Cinnamylideneacetic Acid by Light. C. N. RIIBER (*Ber.*, 1913, **46**, 335—338).—The author has obtained the dimolecular form of cinnamylideneacetic acid by the action of light on cinnamylideneacetic acid.

Cinnamylideneacetic acid was exposed to the action of light until the product had a mean mol. wt. of about 260 in acetone. The complex mixture so obtained was treated with a large quantity of benzene, whereby considerable quantities of oxidation products were isolated. The residue obtained by evaporation of the benzene mother liquor, after successive treatment with cold and boiling benzene, left a white, crystalline residue of *bimolecular cinnamylideneacetic acid*, needles, m. p. 219°, mol. wt. in acetone solution 320, which was purified by solution in methylal and addition of benzene. The acid is very sparingly soluble in the usual solvents. The *silver* salt was examined. The formula $\begin{array}{l}Ph\cdot CH\cdot CH\cdot CH{:}CH\cdot CO_2H\\ CO_2H\cdot CH\cdot CH\cdot CH{:}CHPh\end{array}$ is assigned to the acid, since when oxidised by potassium permanganate in alkaline solution, it yielded oxalic and benzoic acids, and an *acid* which could not be obtained in the pure state but gave a *silver* salt, $C_{18}H_9O_6Ag_3$, and a *methyl* ester, $C_{16}H_{18}O_6$. Since it was stable towards potassium permanganate, its composition is probably represented by the formula

$$\begin{array}{l}Ph\cdot CH\cdot CH\cdot CO_2H\\ CO_2H\cdot CH\cdot CH\cdot CO_2H\end{array}.$$

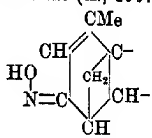
*allo*Cinnamylideneacetic acid is similarly, but more readily, polymerised by the action of light.

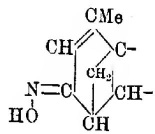
Bimolecular cinnamylideneacetic acid (m. p. 219°) differs greatly from the isomeric acid (m. p. 204°) obtained by the action of light on cinnamylidenemalonic acid (A., 1902, i, 617), particularly in regard to solubility in acetone. The latter acid, when oxidised by potassium permanganate, yielded benzoic and oxalic acids, together with a saturated *acid*, m. p. 134°. α-Truxillic acid could not be isolated. The formula

Ph·CH·CH·CH:CH·CO_2H
CO_2H·CH:CH·CH·CHPh is advanced for the acid m. p. 204°.

H. W.

New Oxime of Santonin. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 796—800).—When nitrosohydroxylamino-β-santoninoxime (Francesconi and Cusmano, A., 1909, i, 724) is heated with an equimolecular quantity of *N*-sodium hydroxide on the water-bath, nitrous oxide is evolved, and an oxime is formed, which is identical with the santoninoxime of Cannizzaro (A., 1886, 73). If, however, nitrosohydroxylamino-α-santoninoxime is similarly treated, a new *santoninoxime* of the same composition is produced; it differs from Cannizzaro's oxime in physical and to a certain extent in chemical properties, and is regarded by the author as representing the oxime of formula II, which is stereoisomeric with the oxime of formula I (Cannizzaro's oxime), adopting the formulæ deduced from the work of Angeli and Marino (A., 1907, i, 321).


(I.)


(II.)

The new oxime crystallises with $1\frac{1}{2}H_2O$, in scales or in lustrous needles; on heating, it becomes red towards 180°, m. p. 230° (decomp.). In addition this α-oxime differs from the β-oxime of Cannizzaro in having a bitter taste, and in yielding the corresponding *santoninic acid*, $C_{15}H_{21}O_4N,3\frac{1}{2}H_2O$, m. p. 80°, when its solution in sodium hydroxide is exactly precipitated with acid. If this acid is kept at 100° for twenty hours, the original oxime is formed. The *hydrochloride* of the oxime crystallises in colourless scales, which change on keeping into large prisms; on heating, the hydrochloride undergoes gradual change until it melts at 168°. With water it yields the oxime, together with santonin and hydroxylamine hydrochloride.

When treated with sodium nitrite and acetic acid, the new oxime yields a *pernitroso*-derivative, $C_{15}H_{18}O_4N_2,H_2O$, which forms prismatic crystals, which become red at 175°, m. p. 197° (with evolution of gas). This compound differs from that obtained from the other oxime in m. p. and in water of crystallisation, but resembles it in giving santonin when heated with alkali, and yielding a blue coloration with a solution of diphenylamine in sulphuric acid.

Treatment of the β-oxime with methyl sulphate yields a *monomethyl ether*, $C_{16}H_{23}O_4N$ (which forms silky, acicular crystals, m. p. 184°), and also another *substance* having the same composition, but crystallising in long, thin needles, m. p. 196°.

Under the same conditions the α-oxime gives a *methyl ether* of the same composition, which forms large, prismatic crystals, m. p. 185°. A mixture of this ether with that of m. p. 184° has m. p. about 160°.

R. V. S.

The Action of Oxalyl Chloride on Polynuclear Hydrocarbons. CARL LIEBERMANN and M. KARDOS (*Ber.*, 1913, 46, 198—212. Compare A., 1911, i, 202, 387, 656; 1912, i, 464).—2 : 4 : 2′ : 4′-Tetramethyldiphenyl, when oxidised by prolonged boiling with sodium dichromate and diluted sulphuric acid, gives in poor yield diphenyl-2 : 4 : 2′ : 4′-tetracarboxylic acid (compare Liebermann and Kardos, A., 1912, i, 465); the same acid is obtained with still more difficulty by the oxidation of 2 : 7-dimethylphenanthraquinone, in which phenanthraquinone-2-carboxylic acid can be isolated as an intermediate product.

Oxalyl chloride reacts with 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethyldiphenyl at the ordinary temperature in carbon disulphide solution in the presence of aluminium chloride, giving a mixture of 1 : 2 : 4 : 5 : 7 : 8-*hexamethylphenanthra*-9 : 10-*quinone*, yellow prisms, m. p. 223—224° (the *monoxime*, yellow flakes, m. p. 178°, when submitted to the Beckmann rearrangement gives a *substance*, possibly the mononitrile of hexamethyldiphenic acid; the *monophenylhydrazone* exists in two forms, α- red needles, m. p. 187°, β- yellow needles, m. p. 143°, which are possibly *cis*- and *trans*-isomerides respectively), with 2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethyldiphenyldicarboxylic acid*, a microcrystalline powder, m. p. 284—285°, which is turned yellow by light. This acid when oxidised in alkaline solution by potassium permanganate is converted into *diphenyl*-2 : 4 : 5 : 2′ : 4′ : 5′ : ? : ?′-*octacarboxylic acid*, a hygroscopic solid which gives a fluorescein reaction when fused with resorcinol; *calcium* salt, very soluble; *silver* salt, colourless; when dried at 110°, the acid loses carbon dioxide and water, giving the *monoanhydride* of *diphenylhexacarboxylic acid*, $C_{12}H_4(CO_2H)_4{<}{\substack{CO\\CO}}{>}O$; the *silver* salt was prepared.

3 : 4 : 5 : 3′ : 4′ : 5′-Hexamethyldiphenyl was prepared from 5-aminohemimellithene (Noelting and Forel, A., 1886, 58; Limpach, A., 1888, 464); in the preparation of this latter substance by heating a mixture of *s*-xylidine hydrochloride and methyl alcohol at 250—260° under 30—33 atmospheres' pressure, a relatively large quantity of acridine bases was obtained as a high boiling, feebly basic mixture, which gave fluorescent solutions in organic solvents; there could be isolated from this mixture a *substance*, m. p. 223°, another substance (probably *tetramethylacridine*), m. p. 172—175°, and a *hexamethylacridine*, m. p. 220—225°; *hydrochloride*, yellow; *platinichloride*, yellow and sparingly soluble. Aminohemimellithene was converted through the corresponding diazonium salt into 5-*iodohemimellithene*, crystals, m. p. 35°, which on heating with finely divided copper (compare Ullmann, A., 1904, i, 725) at 230—250°, loses iodine with the formation of 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethyldiphenyl*, m. p. 132—133°. In an experiment on a small scale, in which hexamethyldiphenyl and oxalyl chloride were kept for six weeks in carbon disulphide solution in contact with aluminium chloride, the product was a mixture of carboxylic acids with a neutral yellow *substance*, doubtless the expected 1 : 2 : 3 : 6 : 7 : 8-hexamethylphenanthra-9 : 10-quinone.

In extension of the earlier result with phthalic acid which was converted by acetyl chloride into phthalyl chloride (Liebermann, A.,

1912, i, 464), it is found that terephthalic and *iso*phthalic acids in like manner with acetyl chloride at 130° give *terephthalyl chloride*, needles or leaflets, m. p. 83—84° (compare Schreder, this Journ., 1874, 990), and *isophthalyl chloride*, prisms, m. p. 43—44°, respectively; in the former case the product is accompanied by a little *terephthalyl acid chloride*, $C_6H_4 \cdot COCl \cdot CO_2H$, needles, m. p. above 300°. D. F. T.

Compounds of Benzaldehyde and Benzonitrile with Antimony Trichloride and Tribromide. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1929—1938. Compare A., 1912, ii, 920, and *ante*).—For benzaldehyde, Haase (A., 1893, ii, 357) gave the m. p. −26°, and Altschul and von Schneider (A., 1895, ii, 206) −13·5°. The author finds that different preparations of the aldehyde melt at temperatures varying from −26° to −15°. This behaviour is probably due to the ready oxidisability of the aldehyde in the air, most samples containing dissolved peroxide and acid. With the systems containing benzaldehyde, difficulties were encountered in determining temperatures lying between the melting point of the aldehyde and the first eutectic point.

Benzaldehyde and antimony trichloride form the compound

$$SbCl_3,Ph \cdot CHO,$$

m. p. 43·5°, crystallising in elongated plates, often united in stellar aggregates. The eutectic point between this compound and the pure trichloride lies at 25°, and corresponds with the composition

$$SbCl_3,0 \cdot 44Ph \cdot CHO.$$

The compound $SbBr_3,Ph \cdot CHO$ forms rhombic plates and crystals resembling rhombohedra, m. p. 41·5°, and the eutectic point,

$$SbBr_3,Ph \cdot CHO\text{–}SbBr_3,$$

lies at 37·8°, and corresponds with the composition

$$SbBr_3,0 \cdot 63Ph \cdot CHO.$$

Benzonitrile has m. p. −13·2° (Hofmann, *Jahresbericht*, 1862, 335, gave −17°, and von Schneider, A., 1896, ii, 290, and 1897, ii, 304, −12·9°).

The compound $SbCl_3,Ph \cdot CN$ crystallises in quadratic plates, m. p. 21·5°, and the eutectic temperatures and compositions of the system are (1) for $Ph \cdot CN\text{–}SbCl_3,Ph \cdot CN$, −19° and $SbCl_3,10 \cdot 6Ph \cdot CN$, and (2) for $SbCl_3,Ph \cdot CN\text{–}SbCl_3$, −15° and $SbCl_3,0 \cdot 59Ph \cdot CN$.

The compound $SbBr_3,Ph \cdot CN$ forms long plates or needles, m. p. 38°, and the eutectic points are 18° for $SbBr_3,8 \cdot 7Ph \cdot CN$ and 35° for

$$SbBr_3,0 \cdot 74Ph \cdot CN.$$

The diagrams of all the above systems have the form typical of the formation from the components of a single stable compound.

T. H. P.

New Synthesis of Syringaldehyde. FERDINAND MAUTHNER (*Annalen*, 1913, **395**, 273—281).—Syringaldehyde is readily obtained in good yield by Guyot's process (A., 1909, i, 935; 1910, i, 40) A mixture of pyrogallol 1 : 3-dimethyl ether, ethyl mesoxalate, anhydrous zinc chloride, and a little carbamide is kept in glacial acetic acid for fourteen days, whereby *ethyl 4-hydroxy-3 : 5-dimethoxyphenyltartronate*, $OH \cdot C_6H_2(OMe)_2 \cdot C(CO_2Et)_2 \cdot OH$, m. p. 60°, is obtained in almost

quantitative yield. The ester, by hydrolysis by boiling aqueous potassium hydroxide, acidification below 10°, and treatment with aqueous copper sulphate finally at the b. p., is converted into *4-hydroxy-3 : 5-dimethoxyphenylglyoxylic acid (syringoylcarboxylic acid)*,

$$OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CO_2H,$$

m. p. 128—129°, yellow needles (p-*nitrophenylhydrazone*, m. p. 225° [decomp.], yellow needles), which yields syringaldehyde by treatment with boiling dimethyl-*p*-toluidine as in Guyot's method. The relative positions of the aldehydo- and hydroxyl groups in the aldehyde are proved by the fact that it yields gallaldehyde trimethyl ether by treatment with methyl sulphate in alkaline solution.

Syringaldehyde forms a p-*nitrophenylhydrazone*, m. p. 216—217°, yellow needles, and an *aldazine*, $C_9H_{12}O_3N_2$, m. p. 208—209°, yellow needles, and reacts with 1-phenyl-3-methyl-5-pyrazolone in hot glacial acetic acid to form 1-*phenyl*-4-p-*hydroxydi*-m-*methoxybenzylidene*-3-*methyl*-5-*pyrazolone*, $C_{19}H_{18}O_4N_2$, m. p. 208—209°, red leaflets, with acetophenone and 33% sodium hydroxide in alcohol at 80° to form, after acidification, 4-*hydroxy*-3 : 5-*dimethoxybenzylidenebisacetophenone*, $C_{25}H_{24}O_5$, m. p. 112—113°, faintly yellow leaflets, and with β-naphthylamine and pyruvic acid in boiling alcohol to form α-p-*hydroxydi*-m-*methoxyphenyl*-β-*naphthacinchonic acid*, $C_{22}H_{17}O_5N$, m. p. 275° (decomp.), yellow needles. C. S.

α-Chloro*cyclo*pentanone and its Derivatives. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, **156**, 332—334).—By passing dry chlorine over *cyclo*pentanone kept at a temperature below 25°, a mixture of substances is obtained, which on fractionation yields 2-*chloro*cyclo*pentanone*, C_5H_7OCl, b. p. 80°/10 mm., D_{14} 1·870, n_D^{14} 1·4782, which on boiling with water or an aqueous suspension of barium carbonate is converted into cyclo*pentanone*-2-*ol*, $C_5H_8O_2$, b. p. 80°/12 mm., D 1·1680. It is very soluble in water, and in solution gives a reddish-brown colour with potassium hydroxide and a violet-red with ferric chloride. It forms a *phenylhydrazone*, yellow needles, m. p. 142—143°, and a *semicarbazone*, a yellow powder decomposing at 170°. This hydroxy-ketone is readily oxidised by 1% potassium permanganate to glutaric acid.

On distilling 2-chloro*cyclo*pentanone either alone or, better, with diethylaniline, it loses hydrogen chloride and is converted into Δ^2-cyclo*pentenone*, a colourless liquid, b. p. 135—136°, which gives a *semicarbazone*, m. p. 214—215°, and an *oxime*, m. p. 52—53°. W. G.

Terpenes and Ethereal Oils. CXIII. Autoreduction of Hydroaromatic Compounds at the Moment of their Formation. OTTO WALLACH and PAUL FRY (*Annalen*, 1913, **395**, 74—86).—β-Methyl-Δ^{β}-hepten-ζ-one and zinc chloride form at the ordinary temperature after two to three weeks a very viscous, brown mass which is probably an additive compound, since it is decomposed into its generators by water. At 100°, however, methylheptenone reacts vigorously in the presence of zinc chloride or phosphoric oxide; hydrogen is not evolved and the product is a complex mixture from

which an oil is obtained by distillation with steam. By distillation this oil yields a very large fraction, b. p. 130—140°, which is not 1 : 3 dimethyl*cyclo*-$\Delta^{1:3}$-hexadiene as stated previously, but is proved to be a mixture of *m*-xylene and 1 : 3-dimethyl-Δ^3-*cyclo*hexene by treatment with 3% potassium permanganate at 0°, whereby the *m*-xylene is unattacked, whilst the 1 : 3-dimethyl*cyclo*hexene is converted into 1 : 3-*dimethyl*cyclo*hexane*-3 : 4-*diol*, $OH\cdot CMe{<}{}^{CH(OH)\cdot CH_2}_{CH_2-CHMe}{>}CH_2$, m. p. 89°. The constitution of the glycol is proved by the fact that it yields 1 : 3-dimethyl*cyclo*hexan-4-one, b. p. 179—179·5°, D^{21} 0·9066, n_D^{21} 1·4464 (*semicarbazone*, m. p. 189°; *oxime*, m. p. 98—99°), by treatment with warm dilute sulphuric acid. This ketone in an impure state (b. p. 176·5°, D^{16} 0·9124, n_D 1·446) has been described by Sabatier and Mailhe, in 1906. By oxidation with chromic and dilute sulphuric acids on the water-bath, it yields a keto-acid (*semicarbazone*, m. p. 136—137°), which is converted into bromoform and β-methyladipic acid by alkaline hypobromite.

Since hydrogen is not evolved and 1 : 3-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene is not obtained by the auto-condensation of the methylheptenone, it follows that one molecule of 1 : 3-dimethyl*cyclo*hexadiene loses hydrogen and changes to *m*-xylene, the hydrogen converting a second molecule into 1 : 3-dimethyl*cyclo*-Δ^3-hexene. C. S.

Synthetic *p*-Dialkylated Dihydroxyquinones and Hydroxyperezone. FRITZ FICHTER, MAX JETZER, and ROBERT LEEPIN (*Annalen*, 1913, **395**, 1—25. Compare A., 1904, i, 678; 1908, i, 658).—The following substances have been prepared by the reaction, as described previously, between sodium, ethyl oxalate, and a fatty ester in ether or benzene. The reaction proceeds more slowly the greater the molecular weight of the fatty acid, and reaches its limit with *n*-decoic ester; ethyl laurate or palmitate do not yield a *p*-dialkylated dihydroxyquinone. 3 : 6-*Dihydroxy*-2 : 5-*diiso*butyl-p-*benzoquinone*, $C_{14}H_{20}O_4$, m. p. 217—218° (in closed tube), red spangles (*diacetate*, m. p. 113·5°, yellow crystals), from ethyl *iso*hexoate, develops a blue coloration in concentrated sulphuric acid and a violet in aqueous sodium hydroxide. 3 : 6-*Dihydroxy*-2 : 5-*diamyl*-p-*benzoquinone*, $C_{16}H_{24}O_4$, m. p. 164°, red leaflets (*diacetate*, m. p. 74°, yellow needles), from ethyl *n*-heptoate; 3 : 6-*dihydroxy*-2 : 5-*dihexyl*-p-*benzoquinone*, $C_{18}H_{28}O_4$, m. p. 154°, red scales (*diacetate*, m. p. 68°, yellow needles), from ethyl *n*-octoate; 3 : 6-*dihydroxy*-2 : 5-*diheptyl*-p-*benzoquinone*, $C_{20}H_{32}O_4$, m. p. 145°, red leaflets (*diacetate*, m. p. 77·5°, yellow needles), from ethyl *n*-nonoate; 3 : 6-*dihydroxy*-2 : 5-*dioctyl*-p-*benzoquinone*, m. p. 141°, red leaflets, from ethyl *n*-decoate. In the colour of their solutions and of their alkali salts, and in their inactivity towards hydroxylamine and ortho-diamines, *p*-dialkylated dihydroxybenzoquinones show a greater similarity to chloroanilic acid than to the unsubstituted dihydroxybenzoquinone. The same is true of their ethers; 3 : 6-*dimethoxy*-2 : 5-*diiso*propyl-p-*benzoquinone*, $CPr^{\beta}{<}{}^{C(OMe)\cdot CO}_{CO\cdot C(OMe)}{>}CPr^{\beta}$, m. p. 142°, prepared from the silver derivative, crystallises in almost black leaflets.

Ethyl iso*valerylacetate*, $CH_2Pr^{\beta}\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 99·5°/12·5 mm., D^{15} 0·964, prepared by hydrolysing ethyl *iso*valerylacetoacetate with aqueous ammonia, is soluble in alkalis, develops an intense red coloration with ferric chloride, yields 1-*phenyl*-3-iso*butyl*-5-*pyrazolone*,

$$CH_2Pr^{\beta}\cdot C{\lessdot}\begin{matrix}CH_2\cdot CO\\ N{-\!\!-}NPh\end{matrix},$$

m. p. 105·5°, with phenylhydrazine, and condenses with resorcinol and concentrated sulphuric acid to form 5-*hydroxy*-4-iso*butylcoumarin*, $C_{13}H_{14}O_3$, m. p. 117°, glistening needles, which dissolves in alkalis with a blue fluorescence.

By treatment with ozonised oxygen, 3 : 6-dihydroxy-2 : 5-dialkyl-*p*-benzoquinones in dry chloroform at 0° do not yield ozonides, but are decomposed in the sense of the equation :

$$C_6R_2(OH)_2O_2 + 6O + 2H_2O = 2H_2C_2O_4 + 2R\cdot CO_2H,$$

the necessary water being produced by the complete oxidation of a portion of the quinone; thus dihydroxydi*iso*propyl-*p*-benzoquinone yields oxalic and *iso*butyric acids, dihydroxy-*p*-xyloquinone yields oxalic and acetic acids (the same products are also obtained by the oxidation of the quinone by alkaline potassium permanganate), dihydroxy-diethyl-*p*-benzoquinone yields oxalic and propionic acids, and dihydroxy-thymoquinone yields oxalic and *iso*butyric acids, acetic acid not being detected.

The study of dialkylated dihydroxybenzoquinones has thrown considerable light on the constitution of perezone (pipitzahoic acid). This substance is converted through the anilino-derivative into hydroxyperezone by Mylius's method (A., 1885, 777, 805). Hydroxyperezone, $C_{15}H_{20}O_4$, m. p. 138—139°, yellowish-red needles, resembles the dialkylated dihydroxy-*p*-benzoquinones in its colour, in the colorations it develops with concentrated sulphuric acid and with aqueous sodium hydroxide respectively, and in its conversion into a *tetra-acetate*, $C_{23}H_{30}O_8$, m. p. 97—98°, colourless crystals, by reductive acetylation. By treatment in chloroform with ozonised oxygen, it yields oxalic acid and not a volatile fatty acid as expected, but $\alpha\beta$-diketobutyric acid, which is isolated and identified by treating its aqueous solution with phenylhydrazine, whereby $\alpha\beta$-diketobutyric acid phenylosazone (completely identified by its conversion by warm alkali into 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone) is obtained. The formation of the diketobutyric acid is accounted for if one of the side-chains in hydroxyperezone is a propenyl group. Consequently, the other side-chain must be a hexyl group, since the sum of the carbon atoms in the side-chains is 9. Hydroxyperezone, therefore, has the constitution

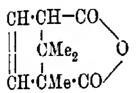
$$C_6H_{13}\cdot C{\lessdot}\begin{matrix}C(OH)\cdot CO\\ CO\cdot C(OH)\end{matrix}{\gtrdot}C\cdot CH{:}CHMe.$$

Since hydroxyperezone readily loses water to form perezinone (Mylius, *loc. cit.*), whilst perezone does not suffer an analogous change, perezone has the constitution $C_6H_{13}\cdot C{\lessdot}\begin{matrix}C(OH)\cdot CO\\ CO{-\!\!-}CH\end{matrix}{\gtrdot}C\cdot CH{:}CHMe$, and perezinone is $\begin{matrix}C(OH){-\!\!-}CO\cdot C{-}CH\\ C(C_6H_{13})\cdot CO\cdot C\cdot CH_2\end{matrix}{\gtrdot}CH$. By reduction with sodium amalgam and aqueous sodium hydroxide at 100°, hydroxyperezone yields

hexylpropenyldihydroresorcinol, $C_{15}H_{24}O_2$, m. p. 140—144°, colourless needles. By similar treatment, dihydroxythymoquinone yields *methylisopropyldihydroresorcinol*, $C_{10}H_{16}O_2$, m. p. 170°, softening at 145°, colourless leaflets. C. S.

Camphor and its Derivatives. XII. JULIUS BREDT (*Annalen*, 1913, **395**, 26—63).—[With J. HOUBEN, P. LEVY, and S. LINK.]—*Methyl 4-chlorocamphorate*, $\begin{matrix} CH_2-CCl(CO_2Me) \\ | \\ CH_2\cdot CMe(CO_2Me) \end{matrix} > CMe_2$, m. p. 56°, b. p. 158°/15 mm., is prepared from 4-chlorocamphoryl chloride and sodium methoxide in methyl alcohol. By slow distillation at 254—285° under ordinary pressure, it yields hydrogen chloride and *methyl dehydrocamphorate*, $C_{12}H_{18}O_4$, b. p. 137°/15 mm., and also methyl chloride and methyl camphanate, the latter decomposition resembling that which occurs during the distillation of the ester of a γ-halogenated fatty acid. *Phenyl 4-chlorocamphorate*, $C_{22}H_{23}O_4Cl$, m. p. 89°, obtained in a similar manner from sodium phenoxide in petroleum (b. p. 70—100°), yields, by slow distillation or by heating with quinoline, only hydrogen chloride and *phenyl dehydrocamphorate*, $C_{22}H_{22}O_4$, m. p. 155°. *Phenyl* dl-4-*chlorocamphorate*, m. p. 74°, yields *phenyl* dl-*dehydrocamphorate*, m. p. 133°, by similar treatment.

By hydrolysis with aqueous methyl alcoholic potassium hydroxide, removal of the alcohol and phenol, and subsequent acidification, phenyl dehydrocamphorate yields *d*-dehydrocamphoric acid, m. p. 202—203°, $[\alpha]_D^{21}$ + 118·6° in chloroform and + 113·8° in alcohol, which is converted into iso*dehydrocamphoric anhydride* (annexed formula), m. p. 185·5—186°, and camphonenic acid by distillation under ordinary pressure. iso*Dehydrocamphoric acid* has m. p. 181—182°, and readily yields the anhydride by treatment with cold acetyl chloride.



Dehydrocamphoric acid yields camphoronic acid by oxidation with dilute nitric acid or alkaline potassium permanganate, and forms a *methyl hydrogen* ester, $C_{11}H_{16}O_4$, m. p. 96°, *silver* salt, $C_8H_{12}(CO_2Ag)_2,H_2O$, and *calcium* salt,

$$C_{10}H_{12}O_4Ca,4H_2O.$$

It does not form an anhydride, and yields the *chloride*, $C_{10}H_{12}O_2Cl_2$, b. p. 139°/13·5 mm., m. p. about 50°, by treatment with phosphorus pentachloride or acetyl chloride. The non-formation of an anhydride and the fact that its chloride reacts with aqueous ammonia at 0° to form the *diamide*, $C_{10}H_{16}O_2N_2,H_2O$, m. p. 191°, colourless needles (compare A., 1912, i, 411), show that dehydrocamphoric acid has something approaching the *cis-trans* configuration. Reference to the tetrahedral model shows that the two carboxyl groups are in what the author terms the *meso-trans* position, in which the spatial separation of the acidic groups is almost as great as in the *cis-trans* modification of the isomeric *iso*dehydrocamphoric acid.

The non-existence of dehydrocamphoric anhydride explains why hydrogen chloride or bromide cannot be eliminated from the C_5-ring of 4-chloro- or bromo-camphoric anhydride.

With S. LINK and TH. FUSSGÄNGER.]—When heated at 100° for

six hours with hydrobromic acid saturated at 0°, *d*-dehydrocamphoric acid yields a mixture of cis-3-*bromocamphoric acid*, m. p. 158—160°, and trans-3-*bromocamphoric acid*, m. p. 232°, of which the former is easily soluble in benzene. The *cis*-acid, which is the chief product of the action of hydrobromic acid at 0°, yields *cis*-camphoric acid, and the *trans*-acid yields *trans*-camphoric acid, by reduction with zinc and glacial acetic and 24% hydrochloric acids. The action of hydrobromic acid at 100° on *dl*-dehydrocamphoric acid yields a mixture of two stereoisomeric dl-3-*bromocamphoric acids*, m. p. 188—189° (decomp.) and 239—240° respectively, of which the less fusible is the chief product, is insoluble in benzene, and yields *trans-dl*-camphoric acid by reduction. Unlike the active acid, *dl*-dehydrocamphoric acid is not attacked by hydrobromic acid at 0°, even after three months.

By boiling with aqueous sodium carbonate and subsequently acidifying, *cis*-3-bromocamphoric acid yields 3-*hydroxycamphorolactone*, $C_{10}H_{14}O_4$, m. p. 228°, whilst *trans*-3-bromocamphoric acid yields trans-3-*hydroxycamphoric acid*, $C_{10}H_{16}O_5$, m. p. 194°, and camphonenic acid, m. p. 155°, identical with that mentioned above and with the unsaturated acid obtained by Noyes from the nitroso-derivative of aminolauronolic anhydride (A., 1906, i, 397). The constitution of camphonenic acid is proved by the formation of camphoronic acid by oxidation with nitric acid or potassium permanganate.

3-Hydroxycamphorolactone boils unchanged, but *trans*-3-hydroxycamphoric acid yields dehydrocamphoric acid and *iso*dehydrocamphoric anhydride by slow distillation. *trans*-3-Hydroxycamphoric anhydride yields only the latter by distillation.

By heating equal molecular quantities of bromine and dehydrocamphoryl chloride at 100° for six hours, decomposing the product with aqueous sodium carbonate, and acidifying, an unsaturated *acid*, $C_9H_{12}O_2$, m. p. 149°, colourless needles, is obtained, which is probably *dehydrolaurolenic acid*.

From the behaviour of the two acids, it is probable that in *cis*-3-bromocamphoric acid the two carboxyl groups are each in the *cis*-position to the bromine atom, whilst in *trans*-3-bromocamphoric acid the bromine is in the *cis*-position to the neighbouring carboxyl and in the trans-position to the other carboxyl group, because lactone formation does not occur by the distillation of its esters, although the halogen is in the γ-position to the carboxyl group. C. S.

Action of Magnesium and Allyl Haloids on Camphor.

METSCHISLAV CHOJN (*J. Russ. Phys. Chem. Soc.* 1912, **44**, 1844—1853).—*Allylborneol* (1 : 7 : 7-*trimethyl*-2-*allyl*-1 : 2 : 2-bicyclo*heptan*-2-*ol*),

$$\begin{array}{l}CH_2\cdot CH-CH_2\\ |\qquad CMe_2\ |\\ CH_2\cdot CMe-C(OH)\cdot CH_2\cdot CH:CH_2,\end{array}$$

obtained by decomposing with water the product of the interaction of magnesium, allyl bromide or iodide, and camphor, is a colourless, viscous liquid with a pleasant camphor-like odour, b. p. 118—119°/17 mm., 120—121°/21 mm., $D_4^{21\cdot8}$ 0·9474, $n_D^{21\cdot8}$ 1·48943, and exhibits the normal molecular weight in freezing benzene or boiling ether. It

unites with two atoms of bromine and, when treated in ethereal solution and in presence of anhydrous sodium sulphate with dry hydrogen chloride at 0°, gives the analogous chloro-derivative, which is converted into the corresponding unsaturated hydrocarbon when heated with dry pyridine.

Oxidation of allylborneol with 1% potassium permanganate solution yields *βγ-dihydroxypropylborneol* (1 : 7 : 7-*trimethyl*-2-*propan*-*βγ*-*diol*-1 : 2 : 2-bicyclo*heptan*-2-*ol*),

$$\begin{array}{l} CH_2\cdot CH-CH_2 \\ \mid \quad\ CMe_2 \mid \\ CH_2\cdot CMe\cdot C(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH \end{array}$$

which forms radiating or beard-like masses of tasteless, odourless, snow-white crystals, m. p. 119—120°, and exhibits normal ebullioscopic behaviour in benzene.

When oxidised with 4% potassium permanganate (4 atoms of oxygen), allylborneol is converted into the hydroxy-acid, *borneolacetic acid*,

$$\begin{array}{l} CH_2\cdot CH-CH_2 \\ \mid \quad\ CMe_2 \mid \\ CH_2\cdot CMe\cdot C(OH)\cdot CH_2\cdot CO_2H \end{array}$$

, which was not obtained in the pure state; the *ammonium*, *silver*, and *calcium* $(+2H_2O)$ salts of the acid were prepared and analysed. T. H. P.

Bupleurol. The Alcohol from the Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 34—40).—This alcohol, which the authors named *bupleurol*, can be isolated by the aid of phthalic anhydride from the higher fractions of the essential oil. It has the composition $C_{10}H_{20}O$, b. p. 209—210°/762 mm., D^{17} 0·8490, n_D 1·4508, and is optically inactive; the substance has a slight, pleasant odour of roses. From its physical properties the substance is probably an olefinic alcohol, and this is supported by the fact that it yields an oily *dibromide*. It forms a *urethane*, which crystallises in lustrous needles, m. p. 45°. Oxidation of bupleurol with chromic acid yields: (1) an *aldehyde*, which shows Schiff's reaction, and gives a *semicarbazone*, m. p. 135°; (2) an *aldehyde*, of which the *semicarbazone* has m. p. 97°; (3) a *ketone* (b. p. 217°, n_D^{25} 1·4419), which yields a *semicarbazone*, m. p. 189—190°; (4) a red oil, b. p. 207°, which is the *ester* of bupleurol and the corresponding *acid*, which was also isolated. Bupleurol is isomeric with citronellol and with androl, and the authors assign to it the formula $CHMe_2\cdot[CH_2]_3\cdot C(CH_2)\cdot CH_2\cdot CH_2\cdot OH$, which is that of a dihydro-derivative of nerol.

When the *phthalic* ester of bupleurol is dissolved in ammonia and treated with silver nitrate, the *silver* salt, $C_{18}H_{23}O_4Ag$, is obtained, m. p. 135°.

In the isolation of bupleurol, a *substance*, $C_{10}H_{16}O$, is als met with; it has an acrid odour, gives a coloration with Schiff's reagent, reduces ammoniacal silver nitrate, and has D 0·9264, $[\alpha]_D$ 14·93°, n_D 1·4909.

R. V. S.

Insoluble Constituents of Ceara- and Rambong-Caoutchouc. CLAYTON BEADLE and HENRY P. STEVENS (*Zeitsch. Chem. Ind.*

Kolloide, 1913, **12**, 46—48).—The influence of the insoluble constituents on the properties of Ceara- and Rambong-caoutchouc has been investigated, and the results compared with those of similar experiments carried out previously with Hevea-caoutchouc (A., 1912, i, 789). "Benzine" was added to the caoutchouc, and the products recovered from the upper clear solution and the lower turbid solution were separately examined, the latter containing practically the whole of the insoluble constituent. The data compared are the nitrogen content, the proportion of free and fixed sulphur in the vulcanised material, and the mechanical properties. Although the relationships involved are of a complicated character, it would appear that the insoluble constituents play an important part in connexion with the vulcanisation of the caoutchouc, and are more or less independent of the percentage content of nitrogenous substances in the caoutchouc. H. M. D.

Artificial Caoutchoucs. II. CARL D. HARRIES (*Annalen*, 1913, **395**, 211—264).—Replies are given to the remarks of Lebedev (A., 1911, i, 959), Kondakov, Ostromisslenski, and Perkin (A., 1912, i, 636) in connexion with the author's first paper (A., 1911, i, 798).

[With MAX HAGEDORN.]—The identity of natural and of artificial caoutchoucs cannot be satisfactorily tested by a comparison of their derivatives except in the case of the ozonides. The products of their decomposition contain similar amounts of lævualdehyde and its acid and diperoxide. Also the comparison of the velocity of decomposition, under proper conditions, of the diozonides and dioxozonides (Harries and Neymann, A., 1908, i, 967; Harries, A., 1912, i, 706) gives satisfactory results. The decomposition curves of the diozonides of Para caoutchouc (purified by twice precipitating its benzene solution by alcohol, and by two extractions with acetone in a Soxhlet apparatus for twelve hours), of gutta-percha, and of artificial caoutchouc obtained by the autopolymerisation of isoprene at 95°, are the same; the decomposition curve of artificial caoutchouc, obtained from isoprene by the acetic acid process, is slightly different. The decomposition curve of "sodium" caoutchouc diozonide is quite different. The same is true of the butadiene caoutchoucs. "Sodium" butadiene-caoutchouc (purified by the alcohol-benzene method) forms a diozonide, the decomposition products of which do not contain a trace of succindialdehyde or lævulaldehyde, and the decomposition curve of which is quite different from that of the diozonide of butadiene-caoutchouc polymerised by heat.

Like natural caoutchouc, artificial "normal" caoutchoucs form diozonides and dioxozonides. Artificial "sodium" caoutchoucs also form diozonides and dioxozonides, although with greater difficulty; the products of their decomposition by water are similar, but the diozonides yield a larger proportion of aldehydes, the dioxozonides a larger amount of acids.

Gutta-percha, purified by alcohol and chloroform and by prolonged extraction with acetone, yields, with washed 9—10% ozone, a *diozonide*, $C_{10}H_{16}O_6$, which so closely resembles the diozonide of natural or of artificial caoutchouc that most probably they are identical. By further treatment with 18% ozone in chloroform, gutta-percha diozonide yields

a *dioxozonide*, $C_{10}H_{16}O_8$, which behaves like the dioxozonide of Para caoutchouc.

The authors have been able to account for a phenomenon which has frequently been observed. Caoutchouc diozonides, prepared apparently in the same manner, frequently yield, by decomposition with water, different amounts of the crystalline lævulaldehyde diperoxide, m. p. 196°; it has now been shown that the quantity of this product increases with amount of dioxozonide in the diozonide.

In partial agreement with Gottlob (A., 1908, i, 436), the authors find that the diozonides of African (Congo) caoutchoucs yield quantities of decomposition products distinctly different from those of the decomposition products of the diozonides of Para caoutchouc, artificial caoutchouc, and gutta-percha. Congo caoutchoucs yield dioxozonides only with difficulty.

[With Wilhelm Schönberg.]—The exhaustive methylation of piperidine is not a suitable method for the preparation of piperylene in quantity. It can be obtained readily as follows: (1) acraldehyde and magnesium ethyl bromide yield by the usual process the alcohol, $CH_2:CH·CHEt·OH$, which is then dehydrated by phthalic anhydride; (2) the alcohol, $CHEt_2·OH$, prepared in the usual manner from ethyl formate and magnesium ethyl bromide, yields Δ^{β}-pentene by distillation with phosphoric oxide; the olefine forms a *dibromide*,

$$CHMeBr·CHEtBr,$$

b. p. 65—70°/15 mm., which is converted into piperylene by the sodium carbonate process at about 600°. This is the best method.

By heating for about fourteen days at 105—110° in an atmosphere of carbon dioxide, piperylene polymerises to "normal" *piperylene-caoutchouc*, $C_{10}H_{16}$, which is elastic and very closely resembles "normal" isoprene-caoutchouc in most of its properties. It forms a *nitrosite*-a, $C_{10}H_{16}O_5N_2$ (?), decomp. 118—122°, yellow powder, insoluble in acetone or ethyl acetate, and a *nitrosite*-c, $2C_{10}H_{15}O_7N_3$, decomp., 162—164°, easily soluble in acetone or ethyl acetate, and an unstable *bromide*, $C_{10}H_{15}Br_3$ (?), decomp. 150—160°, pale yellow, amorphous powder; these three derivatives are almost indistinguishable from the corresponding derivatives of "normal" isoprene-caoutchouc. The ozonides of the two caoutchoucs, however, are quite dissimilar. By treatment with washed ozone in chloroform, piperylene-caoutchouc yields the *diozonide*, $C_{10}H_{16}O_6$, which explodes violently by heating, and exhibits the usual properties of ozonides. It forms a dioxozonide only with very great difficulty. The decomposition curve of piperylene-caoutchouc diozonide is similar to, yet quite distinct from, that of normal caoutchouc diozonide, but the decomposition products are quite different. The former diozonide does not yield lævulaldehyde, but a substance which is most probably methylsuccindialdehyde. Hence "normal" piperylene-caoutchouc (which is a true structural isomeride of "normal" caoutchouc, piperylene being $\Delta^{\alpha\gamma}$-pentadiene) is a derivative of 1 : 5-dimethyl-2 : 6-*cyclo*octadiene,

$$2CHMe:CH·CH:CH_2 \longrightarrow \begin{matrix} CHMe·CH:CH·CH_2 \\ | \qquad\qquad\qquad | \\ CH_2—CH:CH—CHMe \end{matrix} \longrightarrow$$
$$2CHO·CH_2·CHMe·CHO.$$

During the polymerisation of piperylene by heating, a by-product is obtained in the form of a *terpene*, $C_{10}H_{16}$, b. p. 58—59°/11 mm., $D_4^{20.5}$ 0·8313, $n_D^{20.5}$ 1·46916, n_α 1·46620, n_γ 1·48373, which forms a crystalline *bromide*, m. p. 178°, and a white *diozonide*, $C_{10}H_{16}O_6$; the velocity of decomposition of the latter by water at 125° is very great, but definite substances could not be isolated from the products owing to lack of material.

The polymerisation of piperylene by sodium at 60° yields a "sodium" piperylene-caoutchouc which is brittle after purification; it forms a *nitrosite*, decomp. 140—145°, and a *bromide*, the analyses of which do not correspond with the formulæ of the normal compounds.

[By the AUTHOR.]—The proof of the presence of an 8-ring in "normal" caoutchoucs is of fundamental importance in the chemistry of caoutchoucs. To test this point, the velocity of decomposition of "normal" butadiene-caoutchouc diozonide has been compared with that of the diozonide of Willstätter's 1 : 5-*cyclo*octadiene. (A serious difficulty is encountered in separating the "normal" butadiene-caoutchouc from the terpenoid hydrocarbon, C_8H_{12}, obtained as a by-product during the polymerisation. Both substances form almost colourless *diozonides*, $C_8H_{12}O_6$; the diozonide of the terpenoid hydrocarbon is decomposed very rapidly by water at 125°, and the products of decomposition contain hydrogen peroxide, but do not respond to the pyrrole test.) The comparison shows that both decompose at the same rate (at first the "normal" butadiene-caoutchouc decomposes more rapidly, but this is probably due to the presence of a little of the easily decomposable diozonide of the terpenoid hydrocarbon), and yield practically the same amount of succindialdehyde. Since the decomposition curve of 1 : 5-*cyclo*octadiene diozonide is very characteristic, and since the decomposition products of the two diozonides are quite alike in not responding to the hydrogen peroxide test and in containing the same percentage of succindialdehyde, the statement is made with considerable confidence that "normal" caoutchoucs contain an 8-ring.

[With RICHARD SEITZ.]—Although Zelinsky and Gorsky (A., 1908, i, 619) have resolved 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene into its active forms, their method of preparing the substance does not necessarily lead to the formation of a compound of this constitution (compare Harries and Neymann, A., 1909, i, 218). The authors, therefore, have used a method similar to that by which Harries obtained pure $\Delta^{1:3}$-*cyclo*hexadiene (A., 1912, i, 343). 1-Methyl-Δ^3-*cyclo*hexene and bromine in acetic acid yield 3 : 4-*dibromo*-1-*methyl*cyclo*hexane*, b. p. 94—95°/12 mm., which reacts with 33% alcoholic trimethylamine (2 mols.) at about 95° for twenty hours to form 1-*methyl*-Δ^4-cyclo*hexenyl-3-trimethylammonium bromide* or 1-*methyl*-Δ^2-cyclo*hexenyl-4-trimethylammonium bromide*, $C_{10}H_{20}NBr$, m. p. 166—167°. The bromide, whichever constitution it may have, must yield 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene by treatment with water and silver oxide and subsequent distillation. The hydrocarbon agrees well in its physical constants (b. p. 100·5—101·5°, $D_4^{22.5}$ 0·8252, n_α 1·46225, $n_D^{22.5}$ 1·46619, n_γ 1·48519) with Zelinsky and Gorsky's compound (*loc. cit.*). By treatment with unwashed 18—20% ozone in chloroform, it yields a *diozonide*, $C_7H_{10}O_6$,

which is decomposed in ether by copper hydride, yielding probably methylsuccindialdehyde and glyoxal; these substances, however, could not be definitely identified. C. S.

Comparative Researches on the Polymerisation Products of βγ-Dimethylbutadiene obtained Spontaneously and by Heat. CARL D. HARRIES (*Annalen*, 1913, **395**, 264—272).—[With MAX HAGEDORN.]—"Normal" βγ-dimethylbutadiene-caoutchouc, produced by heating βγ-dimethylbutadiene in a closed vessel, yields very readily the diozonide and the dioxozonide, both of which are decomposed by water, giving an almost quantitative yield of acetonylacetone. Kondakov's white, insoluble polymeride, produced by the prolonged keeping of βγ-dimethylbutadiene at the ordinary temperature, also readily forms a *diozonide*, $C_{12}H_{20}O_6$, and *dioxozonide*, $C_{12}H_{20}O_8$, by the decomposition of which by water only about 20% of acetonylacetone is produced. Also the decomposition curves of the two diozonides are very different.

By exposure to air for a few hours, Kondakov's polymeride changes to a yellow, soluble resin. This forms a *diozonide*, $C_{12}H_{20}O_6$, and *dioxozonide*, $C_{12}H_{20}O_8$, by the decomposition of which about 36% of acetonylacetone is obtained.

The author is of opinion that Kondakov's polymeride is not a true caoutchouc, and by analogy, therefore, that the caoutchouc obtained by Pickles (T., 1910, **97**, 1085) by the prolonged keeping of isoprene is not true caoutchouc. C. S.

Chlorophyll. LÉON MARCHLEWSKI (*Annalen*, 1913, **395**, 194—210). —A reply to Willstätter and Isler (A., 1912, i, 710). The author maintains his contention that Willstätter's phaeophytin is chlorophyllan under another name. The heterogeneity of chlorophyllan was established by the author and Malarski (A., 1909, i, 947) before Willstätter (A., 1911, i, 393).

The proportion of the components *a* and *b* in chlorophyll is determined far more conveniently by Marchlewski and Jacobson's method (A., 1912, ii, 705) than by Willstätter and Isler's process (*loc. cit.*). C. S.

Alkaloids of Aconitum Lycoctonum. HEINRICH SCHULZE and ERICH BIERLING (*Arch. Pharm.*, 1913, **251**, 8—49).—A detailed résumé is first given of the work of Hübschmann (*Schweiz. Woch. Pharm.*, 1865, **3**, 269), Dragendorff and Spohn (A., 1885, 403), Einberg (*Diss. Dorpat.*, 1887), Dohrmann (*ibid.*, 1888), and van der Bellen (*ibid.*, 1890) on these alkaloids. The author's results extend, and to some extent confirm, those of Dragendorff and his pupils. It is shown that the alkaloids of this species differ from the typical "aconitines" in not yielding two monobasic acids on hydrolysis.

The coarsely ground roots were exhausted with 94% alcohol, the extract concentrated, and set aside to deposit sucrose, the mother liquor further concentrated, and diluted with three times its volume of water to separate resin and oil, and the filtrate, after extraction with ether to remove the last traces of oil, made alkaline with sodium

hydroxide and the liberated lycaconitine extracted with ether. The alkaline liquor was then shaken with chloroform, and the amorphous alkaloids so obtained freed from traces of lycaconitine by extraction with ether. This partly purified mixture of alkaloids was dissolved in dilute hydrochloric acid (3%), the solution treated with potassium thiocyanate in excess to remove an alkaloid giving an insoluble thiocyanate, and the filtrate made alkaline with sodium hydroxide and extracted with chloroform, which removed myoctonine.

Lycaconitine, $C_{36}H_{46}O_{10}N_2$, $[\alpha]_D^{20}$ +42·47° in alcohol, was decolorised by means of animal charcoal, and thus obtained as a colourless powder, easily soluble in alcohol or chloroform, less so in ether; it is a weak base from which no crystalline derivatives could be prepared. On hydrolysis by water or dilute hydrochloric acid, it yields succinic acid and anthranoyl-lycoctonine. Alkalis hydrolyse it to lycoctonine and lycoctoninic acid.

Myoctonine, $(C_{36}H_{42}O_{10}N_2)_2$, $[\alpha]_D^{20}$ + 44·79° in alcohol, is a colourless, amorphous powder, soluble in alcohol or chloroform, but sparingly so in ether; the solution in alcohol fluoresces bluish-violet. No crystalline derivatives were obtained. On hydrolysis by hydrochloric acid or alkalis, it furnishes the same products as lycaconitine.

The unnamed base giving an insoluble thiocyanate was not analysed; on hydrolysis by alkalis, it also yields lycoctonine and lycoctoninic acid.

Lycoctonine, $C_{25}H_{39}O_7N,H_2O$, m. p. 131—133°, $[\alpha]_D^{20}$+49·64° in alcohol, crystallises in long, colourless needles from dilute alcohol, is a strong base, contains four methoxyl groups and a methylimino-group, and becomes amorphous when dehydrated by drying at 100°/40 mm. The *hydrochloride*, B,HCl,H_2O, m. p. 75° (decomp.), forms colourless prisms; the *hydrobromide*, B,HBr,$2H_2O$, has m. p. 88—89°, and the *perchlorate*, B,$HClO_4$,$1\frac{1}{2}H_2O$, m. p. 68—69° (decomp.), forms heavy prisms. The *methiodide*, B,MeI, m. p. 178°, forms pale yellow needles from alcohol on addition of ether, and the *methochloride aurichloride*, B,Me,$HAuCl_4$, small, heavy, yellow prisms. Lycoctonine contains at least two hydroxyl groups.

Lycoctoninic acid, $C_{11}H_{11}O_5N$, m. p. 179°, forms bright brown needles or leaflets from dilute alcohol, and appears to be succinanil-carboxylic acid (Riedel, A., 1912, i, 774).

Anthranoyl-lycoctonine, $C_{32}H_{44}O_8N_2$, m. p. 154—155°, forms bright brown, glancing leaflets, is easily soluble in chloroform, but sparingly so in other solvents; the solutions fluoresce bluish-violet. The alkaloid contains four methoxyl groups and a methylimino-group. The *perchlorate*, B,$2HClO_4$, alone was obtained crystalline; it forms aggregates of colourless needles, and does not melt completely even at 235°. On hydrolysis by sodium hydroxide in alcohol, the free base yields lycoctonine and anthranilic acid. Anthranoyl-lycoctonine is probably identical with Dragendorff's "lycaconine," but as it is not analogous with the other "aconines," lycoctonine being the corresponding substance in this instance, it is proposed to abandon this name.

The reactions of these alkaloids with the usual alkaloidal reagents and precipitants are tabulated in the original.

Hildebrandt reports that in doses of 0·01 gram, lycaconitine stills the

frog's heart in five hours and myoctonine in seven hours, death occurring three hours later. Lycoctonine causes paralysis after seven hours, but does not still the heart, whilst the action of the relatively insoluble anthranoyl-lycoctonine only becomes apparent after six days. When paralysis of the heart's action does not come on too quickly, all the alkaloids show the characteristic action of the aconitines on the heart. T. A. H.

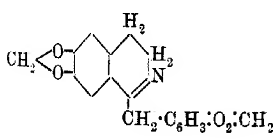
ψ-Laudanine. HERMAN DECKER and THEODOR EICHLER (*Annalen*, 1913, **395**, 377—381).—The reduction of an alcoholic solution of *N*-methylnorpapaverinium phenolbetaine (Decker and Dunant, A., 1908, i, 204) by tin and concentrated hydrochloric acid on the water-bath yields the *stannochloride*, $C_{20}H_{25}O_4N,HCl,SnCl_2$, of a *base*, $C_{20}H_{25}O_4N$, m. p. 111°, which has the constitution:

$$C_6H_3(OMe)_2\cdot CH_2\cdot CH<\begin{matrix}C_6H_2(OH)(OMe)\\ NMe\text{———}CH_2\end{matrix}>CH_2,$$

and is called *ψ-laudanine*, since it differs from laudanine only by the interchange in position of a hydroxyl and a methoxyl group. The *hydrochloride*, *platinichloride*, *chromate*, *picrate*, m. p. 162—163°, and *perchlorate* of the base are mentioned. C. S.

Syntheses of Dihydro*iso*quinoline Derivatives. HERMAN DECKER, WALTER KROPP, HEINRICH HOYER, and PAUL BECKER (*Annalen*, 1913, **395**, 299—320. Compare Pictet and Kay, A., 1909, i, 513; Decker and Kropp, *ibid.*, i, 513).—Derivatives of 3:4-dihydro*iso*quinoline are obtained by the interaction of acyl-β-phenylethylamides and phosphorus pentachloride and phosphoryl chloride in boiling benzene, toluene, or xylene, moisture being carefully excluded. Formo-β-phenylethylamide yields very little 3:4-dihydro*iso*quinoline (*picrate*, m. p. 174—176°), the chief products being β-phenylethylamine and β-phenylethylaminomalon-β-phenylethylamide (Decker and Becker, A., 1911, i, 714). Phenylaceto-β-phenylethylamide, treated as in Decker and Kropp's method (*loc. cit.*), yields *di-β-phenylethylamine* (?), $NH(CH_2\cdot CH_2Ph)_2$, b. p. 220—230°/30 mm. (*picrate*, m. p. 229—231°), and 1-benzyl-3:4-dihydro*iso*quinoline (picrate, m. p. 182°, not 174—175° [Pictet and Kay, *loc. cit.*]). Oxalodi-β-phenylethylamide yields a *substance* (*hydrochloride*, m. p. 191—193°; *picrate*, $C_{24}H_{21}O_8N_5$, m. p. 167—168°, canary-green needles), which is probably 3:4-*dihydroiso-quinolyl-1-carboxy-β-phenylethylamide*, $C_9NH_8\cdot CO\cdot NH\cdot CH_2\cdot CH_2Ph$, since it yields β-phenylethylamine and a derivative of *iso*quinoline by hydrolysis by hydrochloric acid at 120°. Even by energetic treatment, the substance cannot be converted into bis-3:4-dihydro*iso*quinolyl.

Homopiperonoylhomopiperonylamine yields 1-*piperonylnorhydrastinine* (annexed formula), m. p. 136—137°, colourless plates (*picrate*, m. p. 220—223° [decomp.]; *platinichloride*, decomp. 175—180°), together with another base, *picrate*, m. p. 228°.



Phenylacetohomopiperonylamide yields 1-benzylnorhydrastinine

(*picrate*, m. p. 205—206° [decomp.]), whilst *benzohomopiperonylamide*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}COPh$, m. p. 122°, colourless needles, prepared by heating *homopiperonylamine benzoate*, m. p. 115°, yellowish-green needles, at 180° (compare this vol., i, 272), or from homopiperonylamine by the Schotten-Baumann method, yields 1-*phenylnorhydrastinine*, $C_{16}H_{13}O_2N$, m. p. 141°, colourless prisms (*methiodide*, m. p. 241°; *picrate*, m. p. 188—190°).

Formohomopiperonylamide yields by condensation *norhydrastinine*, $CH_2O_2{:}C_6H_2{<}{\begin{matrix}CH_2{\cdot}CH_2\\ CH{=}N\end{matrix}}$, m. p. 90—91°, stout needles (*picrate*, m. p. 237—238°; *hydrochloride*, m. p. 192°; *platinichloride*, decomp. about 240°), the chief product, however, being *homopiperonylaminomalondihomopiperonyldiamide*,

$CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH(CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3{:}CH_2O_2)_2$,

m. p. 124—126° (decomp.), colourless needles, which forms a *picrate*, m. p. 210—211° (decomp.), yellow plates, and *hydrochloride*, m. p. 182—183°. C. S.

Syntheses of Hydrastinine and its *N*-Homologues. Herman Decker (*Annalen*, 1913, **395**, 321—328).—Norhydrastinine (preceding abstract) and methyl sulphate react in toluene at 100° to form 2-*methylnorhydrastinine methosulphate* (*hydrastinine methosulphate*),

$$C_{10}H_9O_2NMe{\cdot}SO_4Me,$$

m. p. 117—119°, pale yellow, crystalline powder, from which hydrastinine is liberated by 15% sodium hydroxide at 0°.

Norhydrastinine in alcohol reacts with benzyl chloride at 50° to form the *benzylochloride*, $C_{10}H_9O_2NCl{\cdot}CH_2Ph$, m. p. 215°, pale yellow powder, and with ethyl iodide to form the *ethiodide*, $C_{10}H_9O_2NEtI$, m. p. 222°, yellow leaflets; 2-*ethylnorhydrastinine picrate* has m. p. 175°. C. S.

Synthesis of Cotarnine and Third Synthesis of Hydrastinine. Herman Decker and Paul Becker (*Annalen*, 1913, **395**, 328—342).—*Formylhomomyristicylamine*, $CH_2O_2{:}C_6H_2(OMe){\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CHO$, m. p. 105—106° (corr.), colourless needles, obtained by heating homomyristicylamine formate at 160—170° for three hours, is converted, by phosphoryl chloride in boiling toluene and subsequently basifying the aqueous solution of the product, into *norcotarnine*,

$$CH_2O_2{:}C_6H(OMe){<}{\begin{matrix}CH_2{\cdot}CH_2\\ CH{=}N\end{matrix}},$$

(*picrate*, m. p. 182—184°, yellow needles), the methiodide of which, m. p. 184—186° (decomp.), is identical with cotarnine hydriodide, and the methosulphate of which is converted into cotarnine picrate (Salway, T., 1911, **97**, 1208) by alcoholic picric acid.

Equal molecular quantities of homopiperonylamine and benzaldehyde react on the water-bath to form *benzylidenehomopiperonylamine*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}CHPh$, m. p. 36°, pale yellow prisms, which is converted by methyl iodide (without a solvent) at 100° into the *methiodide*. The latter is hydrolysed by boiling 95% alcohol or by steam, yielding benzaldehyde and *homopiperonylmethylamine hydriodide*,

m. p. 135—136° (corr.), colourless leaflets. *Homopiperonylmethylamine*, $C_{10}H_{13}O_2N$, b. p. 156—158°/24 mm., pale yellow oil (*carbonate*, m. p. 72—75°; *hydrochloride*, m. p. 183—185°; *picrate*, m. p. 166—167° [corr.]), is converted into formylhomopiperonylmethylamine by heating its formate at 150—160° for seven hours. By condensation with phosphoryl chloride in boiling toluene and basification of the product, the formyl derivative is converted into hydrastinine.

By processes similar to the preceding, *benzylidenehomopiperonylamine* and its *ethiodide*, *homopiperonylethylamine hydriodide*, m. p. 126—128°, white leaflets, and the corresponding *hydrochloride*, m. p. 183—185°, and *picrate*, m. p. 135—136°, orange-red leaflets, *formylhomopiperonylethylamine*, and 2-ethylnorhydrastinine (preceding abstract) have been prepared.

When a certain temperature or duration of heating is exceeded, by-products are obtained in the interaction of benzylidenehomopiperonylamine and an alkyl haloid. Their production is due to the formation of homopiperonyl haloid, which reacts with the benzylidene compound in the same manner as does the alkyl haloid, a derivative of dimethylamine being produced simultaneously. As an illustration of such heterospasis (compare Decker and Fellenberg, A., 1909, i, 116), equal molecular quantities of benzylidenehomopiperonylamine and methyl iodide have been heated in benzene at 140° for six hours and the product has been hydrolysed by steam, whereby *dihomopiperonylamine hydriodide*, $NH(CH_2{\cdot}CH_2{\cdot}C_6H_3{:}CH_2O_2)_2,HI$, m. p. 234—236°, pale yellow prisms, has been obtained. The corresponding *base* has m. p. 72—75° (decomp.).

Moreover, quaternary ammonium haloids are formed when moisture is present during the interaction of benzylidenehomopiperonylamine and an alkyl haloid; in the preceding example, *homopiperonyltrimethylammonium iodide*, m. p. 260—261°, is formed. C. S.

Syntheses of Tetrahydro*iso*quinoline Derivatives. HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 342—362).—Homopiperonylamine or a similar derivative of β-phenylethylamine reacts readily at the ordinary temperature with an equal molecular quantity of an aldehyde to form the alkylidene derivative, which is converted into a tetrahydro*iso*quinoline derivative by a suitable catalyst; homopiperonylamine (or similar base) and the aldehyde, reacting directly in the presence of the catalyst, yield quite different products.

By adding slowly a benzene solution of benzylidenehomopiperonylamine to moderately warm, concentrated hydrochloric acid, the *hydrochloride*, m. p. 309—311°, of 1-*phenyldihydronorhydrastinine*,

$$CH_2O_2{:}C_6H_2{<}\begin{matrix}CH_2\text{—}CH_2\\ \quad\;\; |\\ CHPh{\cdot}NH\end{matrix},$$

m. p. 97—98°, large, hexagonal leaflets, is obtained; the *nitrate* and *picrate*, m. p. 169—170° (decomp.), dark yellow prisms, are described. The same base is produced by reducing 1-phenylnorhydrastinine (preceding abstract) by alcohol and 2·5% sodium amalgam, the solution being kept acid by the addition of glacial acetic acid.

Piperonylidenehomopiperonylamine, m. p. 117—118° (unstable *picrate*, m. p. 143—145°), and *cinnamylidenehomopiperonylamine*, m. p.

61—63°, are respectively prepared from equal molecular quantities of the components on the water-bath.

The slow addition of homopiperonylamine to 20% formaldehyde yields *homopiperonylmethyleneamine*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}CH_2$, a liquid, which is converted by hydrochloric acid on the water-bath into the *hydrochloride*, m. p. 274—276°, of *dihydronorhydrastinine*, $C_{10}H_{11}O_2N$, m. p. 81—83°. This base, the hydrochloride of which is also obtained by reducing norhydrastinine with tin and hydrochloric acid, forms a *hydrobromide*, m. p. 256—258°, *picrate*, m. p. 229—231° (decomp.), and *carbonate*, m. p. 114—115° (decomp. corr.), and reacts in benzene with methyl iodide to form the hydriodide, m. p. 239—241° (Freund and Will record 232°) of dihydrohydrastinine. Dihydronorhydrastinine and methyl sulphate react in benzene to form a crystalline substance, m. p. 135—137°, which is converted, by successive treatment with sodium hydrogen carbonate and hydrochloric acid, into dihydrohydrastinine hydrochloride, m. p. 276—278°. Dihydrohydrastinine in the form of its hydrochloride is obtained directly from homopiperonylamine hydrochloride by heating it with 40% formaldehyde at 130° for three hours. The same hydrochloride is also produced from homopiperonylmethylamine hydrochloride or dihydronorhydrastinine hydrochloride and an excess of 40% formaldehyde at 120°.

The paper closes with an explanation of Eschweiler's process of methylation by means of formaldehyde which is represented by the scheme:

$$RR'NH,HX \longrightarrow RR'N\begin{cases}CH_2{\cdot}OH\\ CH_2{\cdot}OH\\ X\end{cases} \longrightarrow$$

$$RR'N\begin{cases}Me\\ CHO\\ X\end{cases} \longrightarrow RR'NMeX + H{\cdot}CO_2H.$$

This explanation is in harmony with the fact that quaternary ammonium salts are not produced by Eschweiler's method, and, applied to phenols, will account for the frequent occurrence of the methoxyl group in plant substances. C. S.

Synthesis of Pyrroles from Amino-ketones and Ketones or Ketonic Esters. OSCAR PILOTY and PAUL HIRSCH (*Annalen*, 1913, **395**, 63—74).—The synthesis of pyrrole derivatives by Knorr's method of condensing amino-ketones and esters of β-ketonic acids in glacial acetic acid fails in many cases. The authors now find that condensation in alkaline solution is much more satisfactory, and that ketones can be used instead of ketonic esters. An aqueous solution of the amino-ketone hydrochloride is treated with an excess of an alkali hydroxide, the ketone or ketonic ester is added, and the closed vessel is kept at a gentle heat or left for several days at the ordinary temperature; thus aminoacetone yields 2:4-dimethylpyrrole with acetone, *2-phenyl-4-methylpyrrole*, m. p. 152°, with acetophenone, 2:3:4-trimethylpyrrole with methyl ethyl ketone, 3:4-*dimethyl-2-ethylpyrrole*, an oil (*picrate*, m. p. 122·5°), with diethyl ketone, whilst methyl α-aminoethyl ketone yields 2:3:5-*trimethylpyrrole*, b. p. 75·5—76·5°/16 mm. (and tetramethylpyrazine as a by-product), with

acetone, and 2 : 3 : 4 : 5-*tetramethylpyrrole* (*picrate*, m. p. 125—126°), and chiefly tetramethylpyrazine, with methyl ethyl ketone.

Aminoacetone yields ethyl 2 : 4-dimethylpyrrole-3-carboxylate with ethyl acetoacetate, and *ethyl hydrogen* 3-*methylpyrrole*-4 : 5-*dicarboxylate*, $NH<\begin{matrix} CH{=\!=\!=}CMe \\ C(CO_2H)\cdot C\cdot CO_2Et \end{matrix}$, m. p. 196°, with ethyl oxalacetate; by hydrolysis the ethyl hydrogen ester is converted into 3-*methylpyrrole*-4(or 5)-*carboxylic acid*, m. p. 149°, which yields 3-methylpyrrole by heating.

Methyl a-aminoethyl ketone yields *ethyl hydrogen* 2 : 3-*dimethylpyrrole*-4 : 5-*dicarboxylate*, m. p. 201° (decomp.), and tetramethylpyrazine, with ethyl oxalacetate. By hydrolysis the ester yields 2 : 3-*dimethylpyrrole*-4(or 5)-*carboxylic acid*, m. p. 188°, which decomposes at 190—195° in carbon dioxide to form 2 : 3-*dimethylpyrrole*, b. p. 62°/11 mm. (*picrate*, $2C_6H_9N,C_6H_2(NO_2)_3\cdot OH$, m. p. 146·5°).

C. S.

A New Method of Preparing Cyclamine-aldehydes and -alcohols. II. ADOLF KAUFMANN and LOUIS G. VALLETTE (*Ber.*, 1913, **46**, 49—57. Compare A., 1912, i, 655).—In the earlier paper, the aldehydes obtained by the scission of the condensation products of nitrosodimethylaniline with 2-methylquinoline ethiodide or a-picoline methiodide were isolated only as phenylhydrazones; processes are now described for the separation of the aldehydes in a free state.

6-*Methoxylepidine ethiodide*, yellow or brown needles decomposing at 177—179°, gives in dilute aqueous solution a beautiful blue fluorescence; it condenses with nitrosodimethylaniline when heated in alcoholic solution, with the formation of the p-*dimethylaminoanil* of 6-*methoxyquinoline*-4-*aldehyde ethiodide*, green columns, m. p. 214—215°, which gives blue solutions in alcohol and carmine-red in water; this substance dissolves in dilute hydrochloric acid, undergoing scission into *p*-aminodimethylaniline and 6-*methoxyquinoline*-4-*aldehyde ethiodide*, the latter of which can be easily separated as the *phenylhydrazone*, red needles decomposing near 248°.

The dimethylaminoanil of quinoline-2-aldehyde ethiodide (*loc. cit.*) is hydrolysed by mineral acid, and phenylhydrazine precipitates the phenylhydrazone of quinoline-2-aldehyde ethiodide; if the addition of the phenylhydrazine be delayed for a time, the precipitate obtained is a mixture of the above with the *phenylhydrazone* of *quinoline*-2-*aldehyde ethochloride*, red needles, m. p. 180° (decomp.), which on reduction with zinc and dilute hydrochloric acid yields a pungent smelling, oily *base*, together with some aniline.

The hydrolysis of the dimethylaminoanil of pyridine-2-aldehyde methiodide likewise yields the methiodide and *methochloride* of the aldehyde, which can be separated as the phenylhydrazones, that of the methochloride decomposing near 235° after previous fusion in its water of crystallisation near 70°.

If the phenylhydrazone of pyridine-2-aldehyde methiodide, after previous careful removal of water of crystallisation, is heated below its m. p. (244°) under 0·1—0·2 mm. pressure (obtained by Wohl's

method with liquid air and charcoal), methyl iodide is liberated with the formation of *pyridine-2-aldehyde phenylhydrazone*, yellow needles or leaflets, m. p. 180—182°; *hydrochloride*, orange-yellow needles, m. p. 188° (decomp.). The methochloride can also be used for the reaction.

In a similar manner the phenylhydrazone of quinoline-2-aldehyde ethiodide can be decomposed to produce *quinoline-2-aldehydephenylhydrazone*, yellowish-brown needles or leaflets, m. p. 203—204°; *hydrochloride*, red needles, m. p. about 237° (decomp.) (compare von Miller and Spady, A., 1886, 370).

Pyridine-2-aldehydephenylhydrazone undergoes reversible hydrolysis when treated with warm mineral acid, but the addition of dinitrobenzaldehyde causes the removal of the phenylhydrazine by forming a very sparingly soluble phenylhydrazone, and the hydrolysis then proceeds to completion; free *pyridine-2-aldehyde* is a pungent liquid, b. p. 210°/725 mm., which gives the usual aldehyde reactions except with Fehling's solution.

Quinoline-2-aldehyde, obtained by hydrolysis of the phenylhydrazone at 120—130° under pressure, forms colourless tablets, m. p. 70—71° (compare von Miller and Spady, *loc. cit.*). D. F. T.

4-Quinolyl Ketones. II. ADOLF KAUFMANN, MAX KUNKLER, and HEINRICH PEYER (*Ber.*, 1913, **46**, 57—64. Compare A., 1912, i, 1017).—From a comparison of the cinchona alkaloids the conclusion is drawn that a substance of the structure 6-alkyloxy-4(β-dialkylamino-α-hydroxyalkyl)-quinoline should possess properties similar to those of quinine.

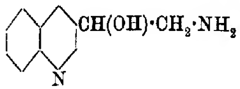
4-Quinolyl methyl ketone has b. p. 99°/0·08 mm., and 4-quinolyl phenyl ketone, m. p. 59°, b. p. 142°/0·12 mm.

6-Ethoxyquinoline (Kaufmann and Peyer, A., 1912, i, 650) readily unites with methyl sulphate with the formation of a yellow solid, the fluorescent solution of which when treated with potassium cyanide yields *4-cyano-6-ethoxy-1-methyl-1 : 4-dihydroquinoline*; the ethereal extract of this substance is oxidised by alcoholic iodine to red needles of *4-cyano-6-ethoxyquinoline methiodide*, m. p. 183—184° (decomp.), which when heated near its m. p. in a vacuum liberates methyl iodide, leaving free *4-cyano-6-ethoxyquinoline* as yellow needles m. p. 118°, which give fluorescent solutions. When treated in benzene solution with an ethereal solution of magnesium methyl iodide the cyano-compound is converted into *6-ethoxy-4-quinolyl methyl ketone*, golden-yellow leaflets or needles, m. p. 80—81°, whilst with magnesium ethyl iodide in an analogous manner, *6-ethoxyquinolyl ethyl ketone*, golden-yellow crystals, m. p. 92°, is produced; both ketones with dilute acids give yellow solutions with a greenish fluorescence.

6-Methoxy-4-quinolyl methyl ketone, dissolved in acetic acid of 50% concentration, is reduced by zinc dust to *6-methoxy-4-quinolyl methyl carbinol*, needles, m. p. 120—121°, which gives a blue fluorescence in dilute sulphuric acid, and an emerald-green coloration with chlorine water and ammonia.

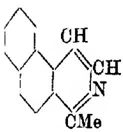
4-Quinolyl methyl ketone in alcoholic solution containing sodium

ethoxide is converted by amyl nitrite into 4-*quinolyl oximinomethyl ketone*, colourless needles, m. p. 237—242° (decomp.), which gives a yellow *substance* with phenylhydrazine, and is reduced by an acid solution of stannous chloride to β-*amino-α-hydroxy-4-quinolylethane* (annexed formula);



hydrochloride, a greyish-white powder, m. p. 208—210° (decomp.); *picrate*, leaflets, m. p. 202°. D. F. T.

A Methylnaphtha*iso*quinoline. AMÉ PICTET and B. MANEVITCH (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 40—47. Compare Pictet and Gams, A., 1909, i, 671).—The preparation of 1-methyl-α-naphtha*iso*quinoline (annexed formula) is described.



A mixture of α- and β-naphthyl methyl ketones was obtained by the addition of aluminium chloride to a solution of naphthalene and acetyl chloride in carbon disulphide. The two isomerides were separated by treatment of their alcoholic solution with a saturated solution of picric acid, whereby the α-naphthyl methyl ketone picrate was precipitated, from which, by decomposition with sodium carbonate, α-naphthyl methyl ketone, b. p. 292—293°, was isolated in 25—30% yield. β-Naphthyl methyl ketone, b. p. 171—172°/12 mm., m. p. 51°, was obtained from the mother liquor, the yield being 12—15%. Attempts to prepare the α-ketone by the action of acetyl chloride on an ethereal solution of magnesium α-naphthyl bromide were less successful.

α-*Naphthyl oximinomethyl ketone*, m. p. 183°, was formed by the gradual addition of amyl nitrite to an alcoholic solution of α-naphthyl methyl ketone in the presence of sodium ethoxide, and was transformed into α-*naphthyl aminomethyl ketone hydrochloride*, m. p. 245—250° (decomp.) by reduction with stannous chloride. The free *base* was unstable.

α-*Naphthyl acetylaminomethyl ketone*, $C_{10}H_7 \cdot CO \cdot CH_2 \cdot NHAc$, m. p. 103°, prepared by the action of acetic anhydride and potassium hydroxide on a concentrated aqueous solution of the above hydrochloride, was reduced by means of sodium amalgam to the corresponding *carbinol*, needles, m. p. 145—146°, which, when treated with phosphoric oxide in boiling xylene solution, was transformed into 1-*methyl-α-naphtha*iso*quinoline*, m. p. 95—96°. H. W.

Amino-Imino-Desmotropy. KURT H. MEYER and HANS SCHLÖSSER (*Ber.*, 1913, **46**, 29—32).—It has already been shown (Meyer, A., 1911, i, 193) that 9-hydroxyanthracene exhibits tautomerism between its enolic and ketonic isomeric structures (anthranol and anthrone), and it is now discovered that similar tautomerism can exist in the anthracene group with 9-aminoanthracene derivatives.

The oxidation of 9-aminoanthracene by amyl nitrite (Kaufler and Suchannek, A., 1907, i, 225) or by bromine in alcoholic solution gives

rise to a substance, m. p. 204—205°, which from its lack of colour and of fluorescence must be dianthronedi-imine,

$$NH:C<\substack{C_6H_4\\C_6H_4}>CH\cdot CH<\substack{C_6H_4\\C_6H_4}>C:NH;$$

it is a diacid base, and the course of the oxidation is evidently analogous to that of anthranol (Meyer, *loc. cit.*). When the substance is boiled for an hour with a methyl-alcoholic solution of potassium hydroxide, it is converted into the isomeric diaminodianthryl,

$$NH_2\cdot C\langle\substack{C_6H_4\\C_6H_4}\rangle C\cdot C\langle\substack{C_6H_4\\C_6H_4}\rangle C\cdot NH_2,$$

golden-yellow leaflets, m. p. 334° (compare Gimbel, A., 1887, 1049), which dissolves in benzene to a solution with a green fluorescence. The same isomeric change can be induced less readily by boiling with acetic acid or by fusion, but the reverse change from the amino- to imino-compound could not be accomplished. D. F. T.

Phenylbenzylidenehydrazine. GEORG LOCKEMANN and FRANZ LUCIUS (*Ber.*, 1913, **46**, 150—152).—Thiele and Pickard (A., 1898, i, 474) obtained by the action of acetic anhydride and zinc chloride or sulphuric acid on phenylbenzylidenehydrazine an isomeric β-modification of the hydrazine, m. p. 136°. On repetition the only product now obtained is α-acetyl-α-phenyl-β-benzylidenehydrazine, m. p. 122°. E. F. A.

Constitution of "Anilipyrine." EZIO COMANDUCCI (*Boll. chim. farm.*, 1912, **51**, 741—743).—Two "anilipyrines" have been described, of which one was supposed to result from the condensation of equimolecular quantities of antipyrine and acetanilide, and the other from two molecules of antipyrine with one molecule of acetanilide. By the method of thermal analysis, the author now shows that these substances are neither compounds nor even mixed crystals, but consist simply of crystalline mixtures. When fused mixtures of the antipyrine and acetanilide are cooled, an eutectic is observed corresponding with 45% of antipyrine and 45°. The behaviour of the "anilipyrines" with solvents supports the above results. R. V. S.

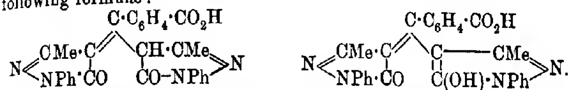
Constitution of "Anilipyrine." LINO METELLO ZAMPOLLI (*Boll. chim. farm.*, 1912, **51**, 780—782. Compare preceding abstract).—Polemical. The author appears to be in agreement with Comanducci's conclusions as now stated. From his preliminary experiments, however, the eutectic temperature is at least 48·5°. R. V. S.

Reaction Products from 1-Phenyl-3-methyl-5-pyrazolone and Phthalic Anhydride. GUSTAV SCHULTZ and GEORG ROHDE (*J. pr. Chem.*, 1913, [ii], **87**, 119—142).—When crystallised from ethyl acetate or acetone, the product, formed by fusing 1-phenyl-3-methyl-5-pyrazolone with phthalic anhydride in equimolecular proportions at 120°, yields an orange-yellow, crystalline *substance*, which becomes red and melts at 202—204°, and on crystallisation from methyl alcohol and acetic acid, or on treatment with aqueous alkalis, loses phthalic

acid and is converted into the red substance first observed by Knorr (*A.*, 1887, 601).

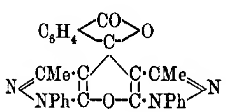
The latter compound is best prepared by boiling the product of the fusion with water until it is completely soluble in chloroform. It crystallises in clusters of dark red prisms or thin, lancet-shaped leaflets, m. p. 208—210° or above, according to the rapidity of heating, and when heated with phthalic acid in acetone or ethyl acetate solution is transformed into the above-mentioned yellow substance.

The constitution of the red substance is represented by one of the following formulæ:



It separates from methyl alcohol and chloroform in red prisms, containing the solvent, and dissolves in aqueous alkalis and alkaline carbonates, forming orange-red salts; the red mono- and di-*silver* salts are mentioned. With methyl-alcoholic hydrogen chloride, it forms a *methyl* ester, $C_{29}H_{24}O_4N_2$, which crystallises in orange-yellow prisms or plates having a bluish glance, m. p. 178—179°, and yields a red *silver* salt, $C_{29}H_{23}O_4N_4Ag$. When heated in nitrobenzene solution or in other solvents of high b. p., the red substance decomposes into 1-phenyl-3-methyl-5-pyrazolone and 1-*phenyl-3-methyl-4-pyrazol-5-onylidenephthalide*, $\begin{matrix}N{=}CMe\\ NPh\cdot CO\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}C_6H_4\\ O\end{matrix}\!>\!CO$. This crystallises in slender, red needles, which sinter at 208°, and have m. p. 212—219°, according to the rapidity of heating. It combines with 1-phenyl-3-methyl-5-pyrazolone in boiling cumene solution to form the original red compound, and is resolved by aqueous alkalis into the ketonic *acid*, $\begin{matrix}N{=}CMe\\ NPh\cdot CO\end{matrix}\!>\!CH\cdot CO\cdot C_6H_4\cdot CO_2H$, which forms lustrous, yellow leaflets of variable m. p. (145—160°), and is reconverted by the action of acetic anhydride into the phthalide.

When warmed with acetic anhydride and a little sulphuric acid, the original red substance is transformed into an *anhydride* (annexed formula), crystallising in slender, colourless needles, m. p. 261°; the reverse transformation may be effected by boiling the anhydride with alcoholic alkali hydroxides. F. B.



The Constitution of the Pyrazolinecarboxylic Acids. AUGUST DARAPSKY (*Ber.*, 1913, **46**, 218—225).—Polemical; a reply to Bülow (this vol., i, 101). D. F. T.

A New Example of the Reversed Pinacolin Rearrangement. HEINRICH BILTZ and KARL SEYDEL (*Ber.*, 1913, **46**, 138—142).—4:5-Diphenyldihydroglyoxalone, $\begin{matrix}CPh\cdot NH\\ CPh\cdot NH\end{matrix}\!>\!CO$, is oxidised by nitric acid to

4 : 5-diphenyldihydroglyoxalone glycol, $\begin{matrix}HO\cdot CPh\cdot NH \\ HO\cdot CPh\cdot NH\end{matrix}\!\!>\!CO$, which in presence of alkaline hydroxides undergoes a normal pinacolin rearrangement into 5 : 5-diphenylhydantoin, $\begin{matrix}CPh_2\cdot NH \\ CO\text{---}NH\end{matrix}\!\!>\!CO$ (compare Biltz, *A.*, 1909, i, 525).

When this hydantoin is energetically reduced with hydrogen iodide and phosphorus, 4 : 5-diphenyldihydroglyoxalone is obtained together with decomposition products, the phenyl group returning to its original place.

The decomposition products include diphenylacetic acid and diphenylmethane, indicating that in the hydantoin the two phenyl residues are attached to the same carbon atom.

On reducing 5 : 5-diphenylhydantoin by distillation with zinc dust, diphenylmethane and benzonitrile are formed, the latter being due to the rearrangement into diphenylglyoxalone which gives rise to benzonitrile when distilled with zinc dust.

Di-*p*-bromo-4 : 5-diphenylhydantoin is very resistant to hydrogen iodide and phosphorus. Only bis-*p*-bromophenylmethane could be isolated from the reaction products; the presence of di-*p*-bromodiphenylacetic acid and of di-*p*-bromodiphenyldihydroglyoxalone was made probable. E. F. A.

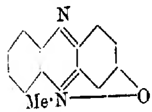
Phenazine. FRIEDRICH KEHRMANN and EM. HAVAS (*Ber.*, 1913, **46**, 341—352).—The authors have obtained good yields of phenazine by the action of *o*-aminodiphenylamine on *o*-nitrodiphenylamine in the presence of anhydrous sodium acetate, and have examined several of its derivatives.

o-Nitrodiphenylamine was obtained in 85—90% yield by heating *o*-chloronitrobenzene, aniline, and anhydrous sodium acetate during twelve to fifteen hours at 215°. Reduction of its alcoholic solution by stannous chloride and hydrochloric acid gave *o*-aminodiphenylamine. For the preparation of phenazine, *o*-nitrodiphenylamine, *o*-aminodiphenylamine, and anhydrous sodium acetate were heated at about 250°, when a violent reaction occurred. The phenazine was isolated by distillation of the crude product, or, better, by treatment with superheated steam; yield, 60—70%. In the absence of sodium acetate, only traces of phenazine could be obtained.

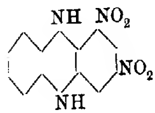
When dissolved in nitrobenzene and treated with methyl sulphate, phenazine yielded *methylphenazonium methosulphate* as greenish-yellow prisms. The corresponding *platinichloride*, $C_{26}H_{22}N_4Cl_6Pt$, and *dichromate*, $C_{26}H_{22}N_4O_7Cr_2$, were analysed, but the *chloride*, *bromide*, and *nitrate* were found to be so readily soluble in water that they could not be precipitated from a solution of the sulphate. When concentrated aqueous potassium iodide was added to an aqueous solution of methylphenazonium methosulphate, an orange-coloured solution was obtained, which, after a short time, deposited greenish-black needles. The latter dissolved readily in hot alcohol with formation of a greenish-yellow solution, which, when rapidly cooled, yielded bluish leaflets, which could be ground to a dirty-green powder.

Analyses of the crystals yielded figures agreeing with those required by the normal iodide, $C_{13}H_{11}N_2I$. The authors, however, are led to the conclusion that this substance is only contained in the yellow solution, and that the crystals probably consist of a quinhydrone salt composed of 1 mol. of methylphenazonium tri-iodide and 2 mols. of methyldihydrophenazine.

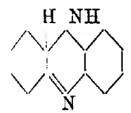
In the presence of air, sodium hydroxide transformed a solution of methylphenazonium methosulphate into phenazine mixed with small quantities of a red *substance*, probably having the annexed formula. Similarly, aqueous ammonia yielded mainly phenazine when brought into reaction with methylphenazonium salts, but, in the absence of water, salts of 3-aminomethylphenazonium were readily obtained. Of these, the following were isolated, namely, the *chloride, bromide*, and *nitrate*, green needles which yielded magenta-red solutions, and the *platinichloride*.



1 : 3-*Dinitrophenazine* was obtained by cautiously heating phenazine with sulphuric acid and rather more than the calculated amount of nitric acid to 130°. It crystallised in yellow needles, which had no definite m. p., but decomposed above 200°. Reduction of this substance by hydrogen sulphide in ammoniacal alcoholic solution led to the formation of dinitrodihydrophenazine (annexed formula), the constitution of which follows from its identity with the compound prepared by Kehrmann and Messinger (A., 1894, i, 55), and by Leemann and Grandmougin (A., 1908, i, 478), from *o*-phenylenediamine and picryl chloride. Attempts to reduce 1 : 3-dinitrophenazine or its dihydro-derivative to diaminophenazine were unsuccessful.



The authors have re-investigated the acetylation of dihydrophenazine (compare Hinsberg and Garfunkel, A., 1897, i, 123; Tichwinski and Wolochowitsch, A., 1905, i, 383; Hinsberg, A., 1905, i, 840). They find that pure acetic anhydride and pure dihydrophenazine yield only a monoacetyl derivative, whilst the diacetyl derivative is immediately formed if a trace of zinc chloride is added. They consider that dihydrophenazine and its diacetyl derivative possess a symmetrical structure, whilst the yellow monoacetyl derivative and dihydrophenazine sulphate are probably derived from the annexed unsymmetrical form.



A solution of dihydrophenazine diacetate in glacial acetic acid was mixed with concentrated nitric acid and warmed on the water-bath, whereby a mixture of 2-*nitrophenazine*, m. p. 214°, and *nitrodiacetyldihydrophenazine*, m. p. 166°, was obtained. The latter substance yielded 3-aminophenazine when warmed with concentrated sulphuric acid.

2-Aminophenazine (compare Fischer and Hepp, A., 1889, 500) was obtained by reduction of an alcoholic solution of nitrodiacetyldihydrophenazine by stannous chloride and hydrochloric acid, oxidation of the tin salt so obtained by ferric chloride solution, and liberation of the base by means of ammonia.

H. W.

New Methods of Preparation of Asymmetric $\alpha\beta$-Naphthazine. FRITZ REITZENSTEIN and FRANZ ANDRE (*J. pr. Chem.*, 1913, [ii], **87**, 97—118).—*as*-$\alpha\beta$-Naphthazine (Fischer and Junk, A., 1893, i, 283) has been prepared (i) from β-naphthylamine by the action of sulphur monochloride or sulphuryl chloride in pyridine solution, and also by distillation over magnesium and barium peroxides; (ii) from α-naphthylamine by heating with calcium oxide, and (iii) by sublimation of aceto-β-naphthylamide over a mixture of barium peroxide and calcium oxide. It forms greenish-yellow crystals, m. p. 278—281°, according to the method of preparation, and yields a dinitro-derivative, m. p. 330—332°, which is reduced by aqueous sodium sulphide to diaminonaphthazine (compare D.R.-P. 166363). When warmed with alcohol and hydrochloric acid, it forms an unstable red *hydrochloride*.

In pyridine solution, sulphuryl chloride reacts with α-naphthylamine, yielding a red *substance*, m. p. 169°, and with aceto-β-naphthylamide to form aceto-1-chloro-β-naphthylamide.

When distilled over a mixture of barium peroxide and calcium oxide, benzidine yields a substance, m. p. 122°, probably identical with the azine, $NH_2\cdot C_6H_4\cdot C_6H_3<\overset{N}{\underset{N}{|}}>C_6H_3\cdot C_6H_4\cdot NH_2$, isolated by Kalb (*Diss.*, München, 1905) from the product obtained by oxidising benzidine. The action of sulphuryl chloride on benzidine in pyridine solution gives rise to a *substance*, m. p. 126°, which is considered to be a chloro-derivative of benzidine or of the above-mentioned azine. F. B.

Synthesis of Two Isomeric Oxytetrazoles from Azoimide and Fulminic Acid. F. CARLO PALAZZO and G. MAROGNA (*Gazzetta*, 1913, **43**, i, 69—80).—The interaction of azoimide and fulminic acid yields, not only the 1-hydroxytetrazole previously described (compare Palazzo, A., 1910, i, 342), but also an isomeride of this substance. Its formation is favoured by a low temperature. The *sodium* salt of *iso-oxytetrazole*, $CHON_4Na,3H_2O$, forms large crystals, which have been described by Rosati (this vol., i, 207). It yields other salts by double decomposition, and gives also a *benzoyl* derivative, which crystallises in needles, m. p. 94°. The sodium salt is stable towards water and alkalis, but with sulphuric acid or with fuming hydrochloric acid suffers a decomposition analogous to that of its isomeride. The *iso-oxytetrazole*, $CHON_3{:}NH$, is obtained by treating the sodium salt with cold, dilute sulphuric acid; it has m. p. 155° (softening a few degrees previously). The decomposition of this substance with sulphuric acid is similar to that of the isomeride, but hydrochloric acid acts somewhat differently. The acid and its salts explode on percussion and also when heated.

The 1-hydroxytetrazole previously described forms when treated with diazomethane an ether containing a methoxyl group; it has m. p. 93—94°. The *iso*oxytetrazole forms an *N*-ether.

The authors consider that the *iso*oxytetrazole probably has the following structure: $\begin{matrix}CH{:}NO \\ | \\ N{=\!=}N\end{matrix}>NH$. They regard the production of these two isomerides from fulminic acid as a further proof of the tautomeric nature of that substance. R. V. S.

Halogen Substitution Products of Azo-dyes. S. WEBER (*Monatsh.*, 1913, **34**, 243—254).—The influence of halogen substitution on the shade and usefulness of some dyes has been systematically studied.

Group A.— *o*-, *m*- and *p*-Chloro-, bromo-, and iodo-anilines, diazotised and coupled with β-naphthol-8-sulphonic acid in sodium carbonate solution, give yellow to red dyes, the *p*-compounds being darker and the *m*-compounds lighter than the *o*-members, whilst the shades deepen from chlorine to iodine.

Group B.—The same bases give redder dyes with α-naphthol-2 : 8-disulphonic acid, but the same generalisations may be made.

Group C.—Aniline, *m*- and *p*-bromoaniline do not couple so readily with 1-amino-β-naphthol-6-sulphonic acid, and the dyes are dark red tinged with blue.

Group D.—2 : 4-Dibromoaniline is less easily diazotised and coupled than the mono-derivatives, but gives deeper colours with the above sulphonates.

The dyes are faster than the unsubstituted analogues, and their colouring power is much enhanced. The ortho- and para-compounds are more valuable than the meta-, and the bromo- and iodo-derivatives are much more effective that the chloro-dyes. J. C. W.

Congo-Red. I. Experimental Part. F. I. BOGOJAVLENSKI. **II. Theoretical Part.** VLADIMIR G. SCHAPOSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1813—1844).—The action of either strong or weak acids (even carbonic acid) on Congo-red results in the replacement of the sodium by hydrogen. With strong acids the action proceeds rapidly and yields a dark blue precipitate, which when washed gives a blue colloidal solution; the latter cannot be freed from admixed impurities by washing or dialysis. This solution of Congo-blue exhibits electrical conductivity, which is, however, probably conditioned by the impurities present. The action of weak acids gives the same product, but in a crystalline condition. Very small crystals of Congo-blue are capable of forming suspensions which closely resemble the colloidal solutions; both the colloidal particles and the crystals carry negative charges, both are coagulated without change of structure by acids or acid salts, and both the colloidal solution and the filtered crystalloidal suspension show Brownian movement under the ultramicroscope, the crystals passing through the filter.

The theoretical considerations of Part II lead to the following conclusions. The change in colour of substantive bisazo-colouring matters is conditioned by change in their intramolecular structure. The red forms of amino- and hydroxybisazo-colouring matters of the Congo-red type correspond with the azoid configuration of the molecules, whilst the blue forms correspond with the quinonoid structure. The instability of these forms and their ready interconversion are regarded as due to the agency of so-called "suspensive" linkings and of mobile hydrogen. T. H. P.

Aniline-Black and Allied Compounds. III. ARTHUR G. GREEN and SALOMON WOLFF (*Ber.*, 1913, **46**, 33—49).—See P., 1912, **28**, 250.

The Density and Solution Volume of Some Proteins. (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Biochem. J.*, 1913, **7**, 92—96).—A comparison was instituted in the case of four proteins, caseinogen, egg-albumin, serum-albumin, and serum-globulin, between the density directly determined with dry specimens and that calculated from the specific gravity of concentrated solutions. The latter is found to be 5 to 8% in excess of the former, showing the extent of shrinkage in volume taking place when these proteins enter into colloidal solution. W. D. H.

The Hydrolysis of Organic Phosphorus Compounds by Dilute Acid and Dilute Alkali. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, **7**, 72—80).—Ethyl dihydrogen phosphate, glycerophosphoric acid, and phytic acid are hydrolysed by acid, but are stable to alkali. Hexose-phosphoric acid and phospho-protein behave so differently to alkali from the other three compounds mentioned, that they are probably not esters. In phospho-proteins, the phosphoric acid is probably united to one of the amino-acids. Hexose-phosphoric acid reduces Fehling's solution, which points to the presence of a functioning aldehyde or ketone group. Some suggestions as to atomic grouping are made to explain the differences in reaction referred to.

W. D. H.

Protein Compounds. WALTER H. EDDY (*Biochem. Bull.*, 1912, **2**, 111—122).—A description is given of protein salts formed by combining organic bases (strychnine, morphine, etc.) with acid reacting proteins (mucoids, nucleoproteins) and by combining the latter with basic reacting proteins, such as histone. It is pointed out that so-called histone, however, is itself probably a protein salt.

W. D. H.

Bilirubin and Hæmin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1913, **83**, 170).—Polemical. A reply to Küster (this vol., i, 210).

E. F. A.

The Action of Pepsin-Hydrochloric Acid on Proteins Partly Digested with Trypsin. VALDEMAR HENRIQUES and J. K. GJALDBÆK (*Zeitsch. physiol. Chem.*, 1913, **83**, 83—92).—Egg-white and caseinogen partly digested with trypsin behave differently when submitted to the subsequent action of pepsin-hydrochloric acid, the former being more readily changed, and the yield of formaldehyde-titratable nitrogen being greater. W. D. H.

Activity of Koji Sucrase [Invertase] in the Presence of Different Acids. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1913, **156**, 261—263. Compare A., 1912, i, 148, 327, 401).—A study of the diastatic activity of the

sucrase, known as "taka-diastase," extracted from the Japanese Koji, in the presence of various acids. This sucrase, unlike those obtained from yeast and ***Aspergillus niger***, shows a maximum activity in solutions the concentration of which with respect to hydrogen ions practically corresponds with neutrality to helianthin, and is independent of the nature of the acid. W. G.

Enzymic Decomposition of Glucosides and Galactosides. HENRY BIERRY (*Compt. rend.*, 1913, **156**, 265—267. Compare A., 1909, ii, 747).—A résumé of the work already published on the enzymic hydrolysis of α- and β-glucosides and galactosides by various ferments. The author finds that the digestive juice of the *Helix* attacks both α- and β-galactosides. The lactase obtained from the intestine of a dog appears to be much more specific in its action, only attacking derivatives of galactose, and of these only the β-derivatives, from which it seems to make a restricted choice in that it hydrolyses lactose itself, but neither α- or β-methyl galactoside. W. G.

The Rate of Destruction of Ptyalin by the Direct Electric Current. W. E. BURGE (*Amer. J. Physiol.*, 1913, **31**, 328—333).—The passage of the direct electric current destroys ptyalin, but this is not due to electrolytic products. The rate of destruction is uniform, and was 2·5% per coulomb for the solutions used. W. D. H.

Resistance of Emulsin to the Action of Heat in Presence of Strong Alcohol. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **7**, 65—67).—In a previous paper (this vol., i, 212), it was shown that the temperature at which emulsin is rendered inactive falls as the concentration of alcohol increases to 50%, but that with stronger alcohols the temperature of inhibition rises with the concentration of the alcohol. It was suggested that this phenomenon is due to the fact that in the stronger alcohols the ferment is precipitated, and in this condition is more resistant to heat. Experiments are now described which prove this contention; thus, it was found that emulsin was scarcely weakened in action when mixed with dry alcohol, and the latter heated slowly to the boiling point and maintained at this temperature during two minutes. In sterilising plants containing enzymes, therefore, it is best to use alcohol of such a strength as to produce a liquid containing about 60% of alcohol when the plants are immersed in it, allowance being made for the water in the plants. T. A. H.

Enzyme Action. III. Action of Manganous Sulphate on Castor Bean Lipase. K. GEORGE FALK and MARSTON L. HAMLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 210—219. Compare Falk and Nelson, A., 1912, i, 523, 593).—Experiments are described which show that when a preparation of castor bean lipase which has been rendered inactive by heating with water is treated with manganous sulphate it becomes slightly active again. In order to explain this behaviour, it is suggested, that although the active enzyme is hydrolysed by the action of hot water, the inactive zymogen present in the pre-

paration is not wholly destroyed, and that the manganous sulphate effects the conversion of the inactive zymogen into active enzyme by a process of oxidation. E. G.

Enzymic Decomposition of Hydrogen Peroxide. IV. PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1913, **83**, 315—337. Compare A., 1911, i, 759; 1912, i, 228; ii, 839).—The action of several proteoclastic and other enzymes on active preparations of catalase has been studied. Trypsin alone destroys the catalase, indicating the protein nature of this substance. The experiments are not in favour of the possible destruction of a protective colloid by the trypsin, thereby destroying the catalase as well. The resistance of catalase to hydrolysis by pepsin suggests that it has a polypeptide structure, but it is possible that the experimental conditions were adverse to the action of pepsin, since the solutions could not be made more than faintly acid.

The gastric juice of the cray fish was especially active in destroying catalase—this confirms its tryptic nature. The action on catalase affords a method of detecting and possibly of measuring tryptic enzymes. Differences are noted in the resistance of blood catalase to the tryptic ferments of vertebrates and of the crayfish, and also in the behaviour of catalases of different origin to the same trypsin.

E. F. A.

Neutralisation of Solutions of Diaminodihydroxyarsenobenzene Hydrochloride. J. CHARLES BONGRAND (*J. Pharm. Chim.*, 1913, [vii], **7**, 49—55).—Theoretically this drug requires 4 mols. of sodium hydroxide to neutralise it by conversion into the disodium derivative. The author shows by means of cryoscopic and electrical conductivity determinations that in dilute solutions, as used in practice, hydrolytic dissociation occurs, and that more than the theoretical amount of sodium hydroxide is then required to maintain the drug in solution, as the disodium derivative. T. A. H.

Phenylstibines. PAUL CARRÉ (*Bull. Soc. chim.*, 1913, [iv], **13**, 102—104).—Magnesium phenyl bromide reacts with antimony trichloride to form triphenylstibine together with the chlorides of phenylstibine and diphenylstibine, the first being almost the sole product when a small proportion of the magnesium compound is used, whilst with 1 or 2 mols. larger quantities of the two latter substances are simultaneously produced. Phenylstibine and diphenylstibine chlorides are decomposed by heat into antimony trichloride and triphenylstibine (compare Michaelis and Günther, A., 1911, i, 1056). T. A. H.

Mercury Dibenzyl. PAUL WOLFF (*Ber.*, 1913, **46**, 64—66).—The description of mercury dibenzyl given by Campisi, in 1865, is erroneous, and endeavours to prepare this substance by the action of sodium amalgam on benzyl chloride have been futile, producing only dibenzyl. The substance has been successfully obtained by the application of magnesium benzyl chloride [see Pope, following abstract].

Mercury dibenzyl is formed, and crystallises in long, colourless needles, m. p. 111° [Pope and Gibson give 104°], which decompose above the m. p. into mercury and dibenzyl. When heated in alcoholic solution with mercuric chloride, *mercury benzyl chloride*, leaflets, m. p. 104°, is obtained; *mercury benzyl bromide* and *mercury benzyl iodide*, prepared in an analogous manner, also form colourless leaflets, m. p. 119° and 117° respectively; *mercury benzyl cyanide*, needles, m. p. 124°, for its formation requires mercury dibenzyl and mercuric cyanide to be heated together in alcoholic solution at 130°. *Mercury benzyl acetate* is produced by the interaction of mercury dibenzyl and mercuric acetate in alcoholic solution, and also of mercury benzyl chloride and silver acetate in alcoholic solution.

Mercury dibenzyl when heated with acetic acid for two or three hours at 170° undergoes decomposition into mercury, toluene, benzyl acetate, and dibenzyl. D. F. T.

Mercury Dibenzyl. WILLIAM J. POPE (*Ber.*, 1913, **46**, 352).—Mercury dibenzyl has been obtained previously to Wolff (preceding abstract) by Pope and Gibson, using the same method (T., 1912, **101**, 735). T. S. P.

Physiological Chemistry.

The Effects of Muscular Exercise in Man. FRANK COOK and MARCUS S. PEMBREY (*J. Physiol*, 1913, **45**, 429—446).—The average composition of alveolar air in healthy men is oxygen, 14·9%, and carbon dioxide, 5·57%. The mean respiratory quotient was 0·9. Directly after muscular exercise the alveolar air contained 14·33% oxygen and 6·52% carbon dioxide; the mean respiratory quotient was 1. During muscular dyspnœa the respiratory quotient affords no definite indication of the metabolism, for the vigorous ventilation of the lungs washes out the carbon dioxide. The administration of oxygen is of value only in pathological conditions. The pulse rate in healthy men at rest varies from 45 to 90 per minute. In a trained man the pulse rate is slower during rest, has a wider range in response to muscular work, and rapidly recovers after exercise. "Second wind" is an adjustment of the respiratory and circulatory systems to the demands of the muscles for an adequate supply of blood; carbon dioxide is the chief factor in effecting the accommodation. W. D. H.

Influence of Calcium and Potassium in the Respiratory Rhythm in Frogs. DONALD R. HOOKER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xvii—xviii).—In the absence of calcium from a perfusion fluid, the respiratory centre is excited; in the absence of potassium it is depressed. In the presence of potassium decrease in the calcium causes depression, and an increase excita-

tion. In the presence of calcium, a decrease in the potassium causes excitation, and an increase causes depression. W. D. H.

The Oxygen Capacity of Blood in Relation to the Concentration of Hæmoglobin. J. H. BURN (*J. Physiol.*, 1913, **45**, 482—488).—No alteration in the oxygen capacity of the blood was discovered when the blood is diluted. Manchot states that it is increased. W. D. H.

Determination of the Constant of the Differential Blood-Gas Apparatus and the Specific Oxygen Capacity of Blood. JOSEPH BARCROFT and J. H. BURN (*J. Physiol.*, 1913, **45**, 493—497). —This apparatus can be best calibrated by the liberation of a known quantity of oxygen from a standard solution of hydrogen peroxide by potassium permanganate. The constant obtained is then higher than by previous methods. Applying this constant, the specific oxygen capacity of hæmoglobin becomes 401·8, the theoretical figure being 400·8 c.c. of oxygen per gram of iron. W. D. H.

The Effect of Exercise on the Dissociation Curve of Blood. JOSEPH BARCROFT, R. A. PETERS, FR. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlv).—The following new terms are introduced. The blood is said to be *mesectic* when the dissociation curve is normal; *pleonectic* when at any given pressure of oxygen the hæmoglobin takes up more of that gas than normal; and *meionectic* when it takes up less. The immediate effect of severe exercise is to shift the curve in the direction of greater acidity, even though the carbon dioxide tension is reduced. After rapid climbing, the curve becomes meionectic; after slow climbing, it remains mesectic. W. D. H.

The Effect of Altitude on the Dissociation Curve of Blood. JOSEPH BARCROFT, MARIO CAMIS, G. C. MATHISON, FR. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlvi).—Although altitudes up to 15,000 feet lower the carbon dioxide alveolar pressure, the blood of the resting subject remains mesectic, for other acids in the blood compensate for the carbon dioxide. Meionexy is brought on by exercise more readily than at the sea level. W. D. H.

The Effect of Carbohydrate-free Diet on the Dissociation Curve of Blood. JOSEPH BARCROFT, G. GRAHAM, and HAROLD L. HIGGINS (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**).—In three out of five cases the curve remained mesectic, although the carbon dioxide tension fell. In two cases it became pleonectic, and the subjects felt knocked up and faint. W. D. H.

The Effect of Moist Heat on the Dissociation Curve of Blood. JOSEPH BARCROFT, MARIO CAMIS, G. C. MATHISON, FR. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlvii—xlviii).—With the wet bulb at 24·5° the carbonic acid

tension fell (as it often does in factories under similar conditions), and the blood became pleonectic. In all these conditions the subject feels well if his blood is mesectic; but variations in either direction produce symptoms of ill-health. W. D. H.

Sugar Loosely Combined in the Blood. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **156**, 110—112. Compare A., 1904, ii, 56; 1907, ii, 562).—The authors have estimated not only the free sugar in the blood of dogs, but also the sugar liberated, after destroying the glycolytic ferment by heating the blood mixed with water at 58° for fifteen minutes, by the addition of emulsin and invertase and keeping the mixture at 39° for forty-five minutes. There is but little or no difference in the amounts of sugar liberated from arterial and venous blood, and but little and in some cases no sugar is liberated from the blood of normal dogs bled for the first time. The amount becomes considerable (up to 50% increase of total sugar) after the physiological equilibrium of the dog has been subjected to marked disturbance by such means as (*a*) severe hæmorrhage, (*b*) intravenous injection of amylase or pancreatin or extracts of liver or pancreas, (*c*) subcutaneous injection of phloridzin. In some cases, also, the intravenous injection of 2 grams of dextrose per kilo. of body-weight was followed by a rise in the amount of sugar liberated by the above method. W. G.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. IV. The Blood-Sugar in Febrile and Dyspnœic Conditions of Man. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 259—267. Compare this vol., ii, 159).—In febrile conditions in man, there is an increase of blood-sugar which at times is quite considerable. There is, however, no parallelism between the increased amount and the rise in the height of the temperature. The hyperglycæmia is caused partly by the hyperthermia and bacterial toxins. In cases of dyspnœa, without high temperatures, where the carbon dioxide content of the blood is increased, hyperglycæmia also occurs. There are, therefore, in certain cases, two distinct causes for increased sugar in the blood, namely, febrile conditions and dyspnœa. Toxic substances, of varied origin, such as tolylenediamine, can also give rise to hyperglycæmia. S. B. S.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. V. The Blood-Sugar in Nephritis, Arteriosclerosis, and Diseases of the Nerves. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 268—277).—Inflammation of the kidneys by itself does not give rise to hyperglycæmia. When such occurs in conjunction with inflammation of the kidneys, it is caused by other factors, which are concomitant pathological conditions, such as arteriosclerosis, dyspnœa, uræmic coma, or bacterial and other toxins. There is no parallelism between the hyperglycæmia and the degree of hypertension. In cases of diseases of the nerves the behaviour of the blood-sugar showed great variations, which depend largely on the seat and character of the affection. S. B. S.

Fibrinsæmia. J. O. WAKELIN BARRATT (*J. Path. Bact.*, 1913, **17**, 301—322).—If thrombin or thrombokinase is injected into the blood-stream of rabbits, separation of fibrin occurs in the circulating blood; the rate of intravascular clotting varies, and is specially readily produced in the right side of the heart; the circulation is by this means mechanically interfered with. W. D. H.

The Sodium and Carbonate Ions in the Serum, and the Question of the "Non-diffusible" Alkali. PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1913, **48**, 278—290).—The method of compensation dialysis was employed in these experiments, the serum being placed in a dialysing membrane, and surrounded by water containing various amounts of salts, the mixtures being kept at the same hydrogen ion concentration as the serum by means of phosphate mixtures. By analysis, after a definite time the amount of salt in equilibrium with that in the serum was ascertained. It was found that the amount of sodium in equilibrium with that of the serum was 0·3260%, whereas the amount in serum determined directly was 0·3057%. There was therefore practically no non-diffusible sodium. The amount of potassium and sodium in equilibrium was found by dialysis to be 0·9214%, whereas the amounts in serum were 0·8532%. In taking into account these two numbers, the volume occupied by the serum proteins must also be considered. The amount of diffusible carbon dioxide was 0·1270%, and that estimated directly in the serum was 0·1270% in one experiment, and similar numbers were obtained from other series. The greater part of the carbon dioxide is therefore diffusible, although a small part is apparently combined as a carbamido-derivative of the proteins. S. B. S.

Rate of Regeneration of Anti-substances [Specially Hæmolysin) and Other Constituents of the Blood after Hæmorrhage. R. A. O'BRIEN (*J. Path. Bact.*, 1913, **17**, 425).—The experiments were made on horses. After bleeding, the constituents of the blood are replaced at differing rates; the volume returns to the normal within forty-eight hours; the proteins commence to be reproduced within twenty-four hours, and the red corpuscles and hæmoglobin within two days. The alterations in leucocytes are irregular, and cannot be correlated with any other factor. The production of anti-substances is as rapid as that of the blood-volume, and suggests that the tissues have a long, persistent habit of forming them in the absence of specific antigens. W. D. H.

Can Lipoids Act as Antigens? JAMES RITCHIE and J. MILLER (*J. Path. Bact.*, 1913, **17**, 429—431).—No evidence was found that lipoids can act in this way. W. D. H.

Hydrolysis of Glycogen by Diastatic Enzymes. Comparison of Glycogen from Various Sources. ROLAND VICTOR NORRIS (*Biochem. J.*, 1913, **7**, 26—42).—On hydrolysis with extract of pig's pancreas, the glycogen is rapidly converted into dextrins and

maltose; the further cleavage of the dextrins is slow and incomplete. The optimum temperature for glycogen hydrolysis is 37°, for starch 40°. When excess of glycogen is present the action is a linear one. The concentration of glycogen has little influence on the initial rate of hydrolysis unless very low concentrations are employed. The action is hindered slightly by the products of hydrolysis; it is favoured by traces of acid. Samples of glycogen from different sources are hydrolysed at different rates at the optimum hydrogen ion concentration; thus, taking dog glycogen as 100, the relative rates of hydrolysis are: rabbit glycogen, 94; oyster, 88; and yeast, 84. The degree of opalescence and the coloration with iodine also vary. The difference may be due to differences in constitution, or to variations in colloidal state. If the glycogens are distinct, the enzymes which affect them should be specific; this is to be tested. W. D. H.

The Secretion of Pancreatic Juice. IWAWO MATSUO (*J. Physiol.*, 1913, **45**, 447—458).—In the preparation of secretin from the intestinal mucous membrane, boiling with 0·6% sodium chloride is as effective as 0·4% hydrochloric acid; organic acids give a smaller yield. Injection of salt solution into the duodenum does not, however, cause a flow of pancreatic juice as the injection of acid does. Secretin was not obtained from any other organ. If two dogs are in vascular connexion, injection of acid into the duodenum of one evokes a pancreatic flow from the other. After the introduction of hydrochloric acid into the duodenum, the duodenal contents contain secretin. Secretin, however, is not absorbed from the intestinal contents, nor does it produce its effects when given under the skin. The view that secretin and "vaso-dilatin" are identical is negatived. W. D. H.

The Rôle of the Pituitary in Carbohydrate Metabolism. LEWIS H. WEED, HARVEY CUSHING, and CONRAD JACOBSON (*Proc. Amer. Physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xiii—xiv).—The posterior lobe of the pituitary plays an important part in carbohydrate metabolism, and its action is controlled by fibres in the cervical sympathetic nerve. Stimulation of this nerve, or of the "sugar centre" in the bulb, or of the pituitary body itself, liberates a hormone which causes glycogenolysis and glycosuria, independently of any possible nervous impulse reaching the muscles or abdominal viscera. W. D. H.

Carbohydrate Metabolism in Ducks. G. B. FLEMING (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xliii—xliv).—Partial removal of the pancreas in ducks raises the amount of sugar in the blood, but does not produce glycosuria. Complete extirpation of the organ has a more pronounced effect on the blood, and sometimes leads to glycosuria. Subcutaneous injection of adrenaline after partial extirpation lowers the percentage of sugar in the blood, and in half the experiments produced glycosuria. The respiratory quotient after fasting averaged 0·72; after feeding on maize, 0·93; after

adrenaline, 0·88. This suggests that the effect of adrenaline is to mobilise carbohydrates; its effect passes off rapidly. W. D. H.

Nitrogen Retention on Feeding with Urea. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **83**, 338—346).—Polemical. A reply to Grafe and Turban (this vol., i, 216). E. F. A.

Protein Metabolism from the Point of View of Blood and Tissue Analyses. VI. Uric Acid, Urea, and Total Non-protein Nitrogen in Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1913, **14**, 29—43).—By the authors' new methods it is possible to measure various degrees of nitrogen retention and urea accumulation due to kidney insufficiency with considerable accuracy. Numerous analyses of the uric acid, urea, and total non-protein nitrogen in the blood are presented both in health and disease. The figures show that there is no relationship between the amount of uric acid and that of urea and non-protein nitrogen. Uric acid may accumulate in the blood, even although urea and other nitrogenous waste products are eliminated quite as well as by normal kidneys; the damage to the kidney in gout may thus affect only its power to eliminate uric acid. Apparently very slight kidney damage may affect its power to excrete uric acid. W. D. H.

The Metabolism of Organic Phosphorus Compounds; Their Hydrolysis by the Action of Enzymes. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, **7**, 43—71).—The action of enzymes is summarised in the following table:

	Pancreas.	Liver.	Intestine.	Castor oil seeds.	Yeast (zymin).	Bran.
Glycero-phosphoric acid	0	0	+	+	+	+
Hexose-phosphoric ,, ...	0		+	+	+	+
Ethyl dihydrogen phosphate .	0		+	+	+	+
Diethyl hydrogen ,,			0	0		
Phytic acid	0	0	0	+	0	+
Nucleic acid (thymus)	0		+		+ ?	+
,, (wheat)			+ ?			
,, (meat)	0		+			
Hydroxymethylphosphinic acid	0		0	0	+ ?	0
Phosphoprotein	+		+		0	0

The most active tissue is the intestinal mucosa. Phytic acid is attacked readily by bran extract only. Phosphoprotein is the only compound hydrolysed by the pancreas. The other compounds in the list are esters; it is evident that the enzyme which attacks them is not lipase. The question whether the phosphatases are single or specific is discussed, and it is suggested that there are mono- and di-phosphatases. Phytase is specific, and if phytin is decomposed in the intestine, this is due to phytase swallowed with the food. It then enters the body as inositol and phosphoric acid. The work of Fingerling and Gregersen is confirmed, that the animal body can and does synthesise its organic phosphorus compounds from inorganic phosphates. W. D. H.

The Rate of Protein Katabolism. E. PROVAN CATHCART and HENRY HAMILTON GREEN (*Biochem. J.*, 1913, **7**, 1—17).—The rise in the output of nitrogen and sulphur after a protein meal is due to katabolism of the actual material ingested, and not to the displacement of "effete" protoplasm from the tissues. This conclusion is based on the ratio of the sulphur and nitrogen in the urine; after ingesting egg albumin the S: N ratio is 1: 8, which is nearly the same as that in egg-albumin. The ratio in starvation when all the urinary constituents must arise from the tissues is 1: 15. The sulphur is more rapidly excreted than the nitrogen; this confirms the view of previous investigators that the sulphur-containing moiety of the protein is the more rapidly katabolised. When protein is superimposed on a low protein diet, a retention of part of the nitrogen takes place. The retained material is apparently stored in the tissues (? muscles) as a pabulum of uniform composition. There was no effect on the output of creatinine.

W. D. H.

The Metabolism of Lactating Women. EDWARD MELLANBY (*Proc. Roy. Soc.*, 1913, *B*, **86**, 88—109).—The post-partum excretion of creatine does not depend on the involution of the uterus. After Cæsarian section, involving amputation of the uterus, it may become more marked than in cases in which the uterus is left intact. Rabbits do not excrete creatine at this period; the explanation of this is not obvious. Eating the placenta will not explain the difference, for cows after eating the placenta, excrete large quantities of creatine. The creatine excretion has some relation to the activity of the mammary gland. The rise in the creatine : creatinine ratio in the first few days after delivery corresponds with the increased activity of the milk glands and the development of milk from colostrum. The increase of weight in healthy breast-fed children is roughly proportional to the amount of creatine in the mother's urine. If the activity of the breasts is delayed after childbirth, so also is the excretion of creatine, and later both develop at the same time. Milk suppression from disease is accompanied by a suppression also of creatine excretion. Feeding with caseinogen does not affect the excretion of creatine in parturient women. The post-partum excretion of creatine is dissimilar from that accompanying acidosis and lack of carbohydrates. Lactose and dextrose added to the diet do not affect it. W. D. H.

Nutrition of the Embryonic Chick. I. The Absorption of Egg-white. HUBERT W. BYWATERS (*Proc. physiol. Soc.*, 1913; *J. physiol.*, **45**, xl—xli).—During incubation, the proteins of the white are not absorbed as quickly as the water, and the ratio of coagulable to uncoagulable protein remains constant; the free sugar is rapidly absorbed; there is no cleavage of carbohydrate from the protein. W. D. H.

The Importance of Phosphorus in the Nutrition of Growing Dogs. ERNST DURLACH (*Arch. expt. Path. Pharm.*, 1913, **71**, 210—250).—Young dogs fed on a diet poor in phosphorus stop

growing, waste, and die. This, however, is not wholly attributable to lack of phosphorus. The absence of other unknown constituents of a diet, possibly of lipoid nature, seems to be a factor, as in Stepp's experiments. Inorganic phosphates appear to be as advantageous for nutrition as phosphatides. W. D. H.

Nutritive Value of the Maize Proteins. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xvi—xvii).—Zein alone produces speedy decline in the growth of rats; it can be made adequate for maintenance by adding tryptophan, or by the addition of another protein. Gliadin suffices for maintenance, but not for growth. Glutelin is adequate for both. W. D. H.

The Influence of Diets upon Growth. F. GOWLAND HOPKINS and ALLEN NEVILLE (*Biochem. J.*, 1913, **7**, 97—99).—A criticism of the work of Osborne and Mendel on the nutrition of young animals on purified proteins (A., 1912, ii, 271). If these workers are correct, the accessory factors in diet (so-called vitamines) are not indispensable. The present experiments do not support this view. On the Osborne-Mendel diet the animals did not grow; but an addition to it daily of 2 c.c. of milk produced growth. W. D. H.

Fasting. PAUL E. HOWE (*Biochem. Bull.*, 1912, **2**, 90—100).—A general discussion of the subject based on the author's work, with special reference to fasting as a therapeutic agent. Long fasts are devoid of benefit, and may be dangerous. Short fasts may be beneficial in certain cases. W. D. H.

A New Method of Drying Tissues and Glands. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, **14**, 27—28).—Instead of using anhydrous salts, the employment of calcium carbide is recommended [compare Masson, T., 1910, **97**, 857]. W. D. H.

A New Type of Artificial Cell. E. NEWTON HARVEY (*Biochem. Bull.*, 1912, **2**, 50—52).—The manner of making cells of about the size of those in the body is described; they contain an aqueous solution of lecithin enclosed in a fine protein membrane, and are suitable for permeability and other biochemical studies. W. D. H.

Pigment of the Corpus luteum. HEINRICH H. ESCHER (*Zeitsch. physiol. Chem.*, 1913, **83**, 198—211).—Willstätter and Escher (A., 1912, i, 125) have shown that lutein, the yellow pigment of egg yolk, belongs to the xanthophyll group of pigments soluble in alcohol. It is now proved that the yellow pigment of the *Corpus luteum* belongs to the carrotene group, $C_{40}H_{56}$, soluble in light petroleum. The process of purification adopted in obtaining 0·45 gram of pigment from 146 kilos. (about 10,000 ovaries) is described. The carrotene is indistinguishable from that obtained from carrots or from green leaves. The yellow pigment of fat is considered to belong to the same class of pigments. E. F. A.

The Lipoids of the White and Grey Matter of the Human Brain at Different Ages. J. Lorrain Smith and W. Mair (*J. Path. Bact.*, 1913, **17**, 418—420).—Five brains were analysed by the methods previously described. The results are given in tables. In the adult the percentage of total lipoids is twice as great in the white as in the grey matter, but the cerebroside is higher, and the phosphatide much lower, than in the grey matter. At birth, there is a low percentage of phosphatides, and more of other lipoids, and the composition is nearly the same throughout the brain. By the age of two, the condition in the adult is nearly, but not quite, reached. W. D. H.

Chemical Changes in Nerve During the Passage of a Nerve Impulse. Shiro Tashiro (*Proc. Amer. Physiol. Soc*, 1912; *Amer. J. Physiol.*, **31**, xxii—xxiii).—The author states that he has constructed an apparatus by which he is able to detect and estimate carbon dioxide in amounts as small as 0·0000001 gram. Resting nerve gives off this gas, and the amount is increased when the nerve is stimulated. W. D. H.

The Utilisation of Sugars by the Normal Heart. Hugh Maclean and (Miss) Ida Smedley (*J. Physiol.*, 1913, **45**, 462—469). —Locke's method for the isolated heart was employed. The utilisation of sugar by the heart is not confined to dextrose; mannose is also used, and so is lævulose, especially in the dog's heart. Maltose, lactose, and sucrose are not utilised, and galactose very slightly. In the cat, sugar does not disappear from the circulating fluids until about three hours after perfusion commences; it is assumed that the reserves in the heart are utilised first. It was found difficult to secure asepsis during the experiments. W. D. H.

The Behaviour of the Diabetic Heart towards Sugar. Hugh Maclean and (Miss) Ida Smedley (*J. Physiol.*, 1913, **45**, 470—472). —The normal power to consume sugar is absent or nearly so in the heart of the depancreatised dogs; the power can be sometimes restored by the addition of pancreatic extract. These experiments confirm those of Knowlton and Starling. W. D. H.

The Storage and Release of Glycogen. Kuniomi Ishimori (*Biochem. Zeitsch.*, 1913, **48**, 332—346).—The methods of experiment were both chemical (estimation of glycogen) and histological (with use of Best's carmine method). Rabbits were employed. It was found that the course of disappearance of glycogen produced by starvation was different from that produced by *piqûre*. In the former case, it disappears from the periphery of the lobe, towards the centre, and glycogen as such could not be detected outside the liver cells. In the latter case, all the liver cells are affected alike, and glycogen could be detected in the lymph spaces and circulation. Intravenous infusion of dextrose and lævulose caused an increase in the glycogen content of the liver. This was not the case with lactose, galactose, and sucrose. S. B. S.

The Character of the Fat Formation in Organs after Phosphorus Poisoning. HANS LEO (*Biochem. Zeitsch.*, 1913, **48**, 297—301).—The author recapitulates the evidence in favour of the new formation of fat in the liver of animals poisoned with phosphorus, which probably exists in this organ in addition to the transported fat. S. B. S.

Fat Formation under the Influence of Phosphorus. HANS LEO and W. TRASCHENNIKOV (*Biochem. Zeitsch.*, 1913, **48**, 302—312). —The majority of the experiments were carried out with the livers of rabbits, part of which were incubated under precautions for strict asepsis in Ringer's fluid alone as a control, and part under the same conditions with the addition of phosphorus. After incubation, the amount of ether-soluble substances, or higher fatty acids, were estimated. In eight experiments the addition of phosphorus caused an increase in fatty substances. In three experiments the results were of a negative character. S. B. S.

Fat Formation in the Surviving Liver. HANS LEO and C. BACHEM (*Biochem. Zeitsch.*, 1913, **48**, 313—327).—The effect produced on the fat content of livers by perfusing both foodstuffs and toxic substances through the surviving organs was investigated. Livers both of cold-blooded and warm-blooded animals were used. and the Langendorff apparatus was employed. In five experiments with foodstuffs (sugar or nutrose in Ringer's fluid), the results indicated fat formation, whereas in four experiments the results were negative. All the experiments with livers of warm-blooded animals yielded a positive result. The addition of alcohol and potassium arsenite showed no fat formation. In four experiments with diphtheria toxin, one gave a negative, one a doubtful result, and two others indicated fat formation in the liver. Out of fourteen experiments with phosphorus water, ten gave negative, and four positive results. The general result indicates that there is no new fat formation in the liver as the result of the action of phosphorus, although two of the experiments with livers of warm-blooded animals indicated an increase in fats. It is suggested that in the case of cold-blooded animals, the rate of fat formation is too slow for it to be possible to obtain an increase in the amount of fat under the conditions of experiment employed. S. B. S.

The Delayed Heat-Production of Muscles Stimulated in Oxygen. ARCHIBALD V. HILL (*Proc. physiol. Soc.*, 1912; *J. Physiol.*, **45**, xxxv—xxxvii).—By improved methods the author's previous conclusion is confirmed that heat-liberation occurs largely (probably 40%) after muscular contraction; oxygen is mainly of use in repair. The action of oxygen is rapid. W. D. H.

The Physico-chemical Basis of Striated Muscle Contraction. II. Surface Tension. WILLIAM N. BERG (*Biochem. Bull.*, 1912, **2**, 101—110. Compare this vol., i, 132).—Bernstein's calculations

of the surface energy changes in contracting muscles are criticised. The energy expended is far greater than any changes in surface tension can furnish. The use of mathematics in biology is regretted, if the treatment, as it so generally does, lacks definiteness; formulæ are often stated with no information as to their use or application to the problem under discussion. W. D. H.

Osmotic and Colloidal Imbibition by Muscle. REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, **48**, 217—224).—The experiments were carried out with the gastrocnemius muscle of frogs, and the changes after various treatments are measured by estimating the gain or loss of weight of the muscles. It was found that the addition of proteins to salt solutions in which the muscles are immersed has no appreciable effect on the water exchange between the tissues and the surrounding fluid. If the stimulability of muscle is destroyed by treatment with acid, its ordinary osmotic functions can still be detected, even for a long period after the loss of stimulability. If, on the other hand, the stimulability is destroyed by heat coagulation, the osmotic properties are lost. S. B. S.

The Chemical Pathology of Muscle. The Influence of Disuse Atrophy in the Partition of Nitrogen and Phosphorus in the Muscle. GEORGE GRUND (*Arch. expt. Path. Pharm.*, 1913, **71**, 129—141).—Full analytical details of paralysed in comparison with healthy muscle are given. The most important result appears to be an increase of phosphorus in protein union in the paralysed muscles. W. D. H.

The Creatine Content of Normal Muscle and its Relation to Urinary Creatinine. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **14**, 9—26).—The creatine content in muscle is constant in a given animal, but differs in different animals; the percentages are 0·52 for the rabbit, 0·45 for the cat, 0·37 for the dog, and 0·39 for man. The creatinine elimination bears a distinct relation to the muscular creatine content. W. D. H.

Occurrence of Alizarin in the Shell of the Crab. FRIEDRICH KORNFELD (*Chem. Zeit.*, 1913, **37**, 71).—A reply to Grandmougin (this vol., i, 132) describing further experiments which support the view expressed previously (*Chem. Zeit.*, 1912, **36**, 59) that crab-shells contain alizarin. T. A. H.

Normal Presence of Bromine in Human Organs. A. LABAT (*Compt. rend.*, 1913, **156**, 255—258. Compare Pribram, 1907, ii, 111).—The various organs of human beings, who had not taken bromine medicinally for several years, were pulped, dried, and incinerated with calcined magnesia, and the ash examined for bromine by the method of Denigès and Chelle (this vol., ii, 72). Bromine could not be detected in the kidney, spleen, liver, heart, or blood serum or coagulum of the four subjects examined, but in

all cases was found in the brain, thyroid gland, and urine. The amount of bromine present in the thyroid gland is considerably less than the iodine. W. G.

The Presence and Distribution of Manganese in Animal Organs. GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Ann. Inst. Pasteur*, 1913, **27**, 1—11).—Manganese has been found in all the animal products examined with the exception of the white of egg. The variations in amount are only small in a given organ of a given species. There is, as a rule, very little difference in the content of manganese in organs of animals of different species belonging to the same class (birds, fishes, mammals). Amongst functional organs the highest amount of manganese has been found in the uterus of birds (0·786—2·201 mg. per 100 grams). Next in order are the liver, then the kidneys. The organs of birds are richer than those of mammals. Smallest amounts are found in muscular tissue, nervous tissue, and (least of all) the lungs, which only contain 0·006 to 0·023 mg. per 100 grams. The grey nervous matter contains more than the white, and heart muscle more than the muscles of the limbs. The mucous membranes contain more than the underlying muscular tissue. Feathers and nails contain relatively large quantities of manganese (0·111 to 3·214 mg. per 100 grams), whereas the teeth contain little. Milk contains very little manganese, and in the egg the whole of the metal is in the yolk. The general results indicate that manganese plays some physiological rôle as a catalyst. S. B. S.

The Origin of Oxalic Acid in the Animal and Human Organism. LESLAW WEGRZYNOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 112—142).—Proteins have no influence on the formation of oxalic acid in the body, neither have carbohydrates and fats (also glycerol). The ordinary articles of diet have no influence, direct or indirect, on oxalic acid formation. The organism evidently has a very limited capacity to form this acid at all. W. D. H.

Histones and Nucleohistones. Their Detection in the Fluids of the Organism. GEORGES PATEIN (*J. Pharm. Chim.*, 1913, [vii], **7**, 55—60).—A description is first given of the characters of histones and nucleohistones, and by the application of Goubau's method it is shown that these substances do not occur in the blood serum of man or the horse, or in ascitic fluid containing chyle. The conclusion is drawn therefore that histones and nucleohistones, which have only been found in such organs as the thymus and the spleen, are fixed there, and cannot be carried away by the body fluids.

Acetoglobulin tested in the course of these experiments was found to contain only traces of phosphorus, and sometimes none. T. A. H.

Relation of Pulse Pressure to Renal Secretion. ROBERT A. GESELL (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol*, **31**, xxviii—xxix).—In dogs alterations of the arterial pressure, espe-

cially if suddenly produced, cause diminution in the secretion of urine, and if albuminuria is present, this is increased. W. D. H.

Excretion of Nitrogen after Ligaturing the Renal Arteries. J. D. PILCHER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xii—xiii).—Tying one branch of each renal artery has no effect; but if three-fourths of the arterial supply is cut off, anorexia and loss of weight occur, and the nitrogen output is greater than the intake. The urine secreted contains neither protein nor casts.
W. D. H.

Beri-Beri. The Action of Certain Purine and Pyrimidine Derivatives. CASIMIR FUNK (*J. Physiol.*, 1913, **45**, 489—492).—Certain purine and pyrimidine derivatives have marked beneficial effect on pigeons suffering from polyneuritis; no relation, however, between the action and chemical structure can be discovered. Experiments with allantoin suggest that pigeons are not able to convert uric acid into allantoin. W. D. H.

Colloidal Nitrogen in the Urine of a Dog with a Breast Tumour. MAX KAHN and JACOB ROSENBLOOM (*Biochem. Bull.*, 1912, **2**, 87—89).—Töpfer states that the urine of cancer patients is rich in "extractive substance," which includes "colloidal nitrogen." The colloidal nitrogen was more abundant in a dog with a tumour in the breast than in normal dogs. The nature of the tumour was doubtful. W. D. H.

The Comparative Mineralisation of Cancareous and Relatively Healthy Portions of the Liver. ALBERT ROBIN (*Compt. rend.*, 1913, **156**, 334—336).—Cancareous portions of liver are richer in total inorganic matter than healthy parts, and whilst some of the inorganic constituents, namely phosphorus, sodium, potassium, magnesium, and silicon, are in excess, others, namely, calcium and iron, are deficient. A similar deficiency in calcium and iron is found in tuberculous lungs, potassium again being in excess. Whilst in the cancareous liver relatively more sodium than potassium is fixed, the reverse is true in the case of a tuberculous lung. From the experimental results, it seems probable that silicon, phosphorus, sodium, potassium, and magnesium are agents of neoplastic cell construction, not specifically for cancer, whilst iron and calcium are rather agents of organic defence. W. G.

Hæmatogenous Jaundice. GEORGE H. WHIPPLE (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xi—xii).—If hæmoglobin is given intravenously to a normal dog, it appears in the urine, and one or two hours later bile pigment occurs there also. The same occurs after an Eck fistula, and also when the hepatic artery is tied in addition. This is taken to prove that bile pigments can be formed in the blood, probably by the agency of the endothelial cells. W. D. H.

The Swelling of Connective Tissues. EDWIN HAUBERRISSER and FRITZ SCHÖNFELD (*Arch. expt. Path. Pharm.*, 1913, **71**, 102—128). —Martin Fischer's theory of œdema renders necessary an investigation of the part played by different ions (for example, in Ringer's solution) in causing swelling. A large number of observations on this line are recorded, and the principal conclusion is stated to be that sodium ions do not act differently from the others. The experiments were in the main performed on the ligamentum nuchæ. W. D. H.

Antagonism between Salts and Anæsthetics. III. Parallel Decrease in the Stimulating, Permeability-increasing, and Toxic Actions of Salt Solutions in the Presence of Anæsthetics. RALPH S. LILLIE (*Amer. J. Physiol.*, 1913, **31**, 255—287. Compare A., 1912, ii, 280, 468).—Pure isotonic sodium chloride solutions produce in *Arenicola* larvæ stimulation of the muscles, arrest of ciliary action, and a general toxic action. These results are lessened or prevented by anæsthetics; the stimulating action and permeability increase undergo a parallel diminution. The essential effect of anæsthetics is an alteration in the plasma membranes of the cells affected. The degree of resistance of these membranes is intimately dependent on the state of their lipoid constituents. W. D. H.

Behaviour of Mercury in the Human and Animal Organism on the Usual Therapeutic Methods of Application. New Method for the Estimation of Mercury in Urine and in the Tissues. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **83**, 249—303).—Contains a critical summary of the methods of estimating mercury in urine with a full bibliography. A method is described of destroying the urine by evaporating with potassium chlorate and hydrochloric acid and so converting the mercury into chloride. The solution is filtered and electrolysed in a special apparatus between a cathode of gold foil and a gas carbon anode. The mercury is deposited on the gold, which is rinsed, dried and weighed, and heated to volatilise the mercury, the weight of which is determined by difference.

The skin is equally able to take up volatile and non-volatile mercury ointments; the ointment base has an accelerating influence on the resorption. The separation of mercury in the urine has been studied after internal administration, and also after intramuscular and intravenal injection of mercury salts. In the latter case the separation is materially faster. The addition of potassium iodide to the mercury salt is shown to diminish the excretion of the mercury. E. F. A.

The Influence of Alcohol on Reflex Action in the Frog. IDA H. HYDE, RUTH SPRAY, and IRENE HOWAT (*Amer. J. Physiol.*, 1913, **31**, 309—317).—The reflexes investigated were from certain skin areas. If the dose of alcohol used is sufficient to produce any effect at all, it is always a depressed or slowed response, never the opposite. W. D. H.

Glyconeogenesis. II. The Formation of Dextrose from Valeric and Heptoic Acids. A. I. RINGER and L. JONAS (*J. Biol. Chem.*, 1913, **14**, 43—52).—In phloridzinised dogs, the administration of formic acid leads to no increase in the output of dextrose; butyric and hexoic acids increase the excretion of acetoacetic and β-hydroxybutyric acids, but not that of sugar. Valeric and heptoic acids give rise to dextrose, probably because propionic acid is an intermediate substance in their katabolism, after undergoing β-oxidation. Fatty acids with an uneven number of carbon atoms can therefore give rise to dextrose. W. D. H.

The Fate of Indole-ethylamine [3-β-Aminoethylindole] in the Organism. ARTHUR J. EWINS and PATRICK P. LAIDLAW (*Biochem. J.*, 1913, **7**, 18—25).—If 3-β-aminoethylindole (Ewins, T., 1911, **99**, 270) is perfused through the surviving liver of rabbits and cats, it is converted into indoleacetic acid. If it is given by the mouth to dogs, 30% of it is excreted as *indole-3-acetylglycine*, $C_6H_4{<}_{NH\cdot CH}^{\quad}{>}C\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ (*picrate*, m. p. 145°) (for which the authors suggest the name *indoleaceturic acid*), which is formed from indoleacetic acid by combination with glycine. Neither 3-β-aminoethylindole nor indoleacetic acid affects the output of kynurenic acid. W. D. H.

Influence of Intraperitonal Injection of Adrenaline on the Partition of Urinary Nitrogen in a Dog. JACOB ROSENBLOOM and WILLIAM WEINBERGER (*Biochem. Bull.*, 1912, **2**, 123—127).—The nitrogen partition was not affected. W. D. H.

Action of Drugs on the Lungs. DENNIS E. JACKSON (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xxvi—xxvii).—Pilocarpine causes bronchial constriction, which is relieved by adrenaline. The nerve endings are sensitive to the latter drug after atropine. Agaricine slightly depresses the constrictor nerve-endings. In small doses the pilocarpine effect is followed by dilatation, but the second effect does not occur if the suprarenals are tied off. Tyramine also causes dilatation, but this is a secondary adrenaline effect also. Choline hydrochloride acts like adrenaline, so also do trimethylamine hydrochloride and 3:4-dihydroxyphenylethylmethylamine in less degree. W. D. H.

The Pharmacological Susceptibility of the Peripheral Vascular Tonus of the Frog. HANS HANDOVSKY and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 89—101).—The Läwen Trendelenburg preparation of the frog was used. Vaso-constrictors fall under three types: (1) adrenaline, which affects post-ganglionic nerve fibres; (2) nicotine, which affects pre-ganglionic and ganglionic structures; and (3) barium, which affects the muscular fibres. The dilators, tyramine, histamine, and Witte's peptone, all

act in the same way. They dilate the vessels after adrenaline is used; tyramine hinders nicotine action. Choline acts as a dilator.
W. D. H.

Nicotine and Calcium Salts. W. BURRIDGE (*Proc. physiol. Soc.*, 1912; *J. Physiol.* **45**, xxxvii—xxxix).—Isotonic solutions of sodium oxalate, sulphate, fluoride, pyrophosphate, and citrate produce a slow tonic contraction of the frog's sartorius muscle. This is attributed to the removal of calcium. Nicotine produces, in addition, twitchings, which are largely abolished by curare. W. D. H.

The Effect of Strychnine on Frogs without Heart and Lymph Hearts. SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xix—xx).—Abel considers that the effect of drugs in a frog without a heart is brought about by the continued activity of the lymph hearts. This is not so for strychnine. Strychnine convulsions set in after thirty to fifty minutes when the lymph hearts are all destroyed. W. D. H.

Muscle Physiology. Action of Veratrine on Striated Muscles in Warm-blooded Animals. G. QUAGLIARIELLO (*Zeitsch. Biol.*, 1913, **59**, 441—468).—Veratrine causes two contractions, the second of which lasts longer. It also causes fibrillary twitchings in small doses. Variations in the curves obtained with varying doses are illustrated by reproductions of the tracings. W. D. H.

The Action on Man of Vapours of Technical and Hygienic Importance. XXX. Nitric Acid. KARL B. LEHMANN and LUDWIG DIEM (*Arch. Hygiene*, 1913, **77**, 311—322).—The toxic symptoms on animals of air contaminated by nitric acid are not particularly characteristic, and are similar to those produced by other irritant substances, such as hydrogen chloride, sulphur dioxide, etc. Three cats died in the respiration chamber in 35 to 120 minutes in the presence of 0·5 to 0·73 mg. of the acid to 1 litre of air. Two animals recovered after doses of 0·43 to 0·5 mg., and one survived until the next day with a dose of 0·88 mg. after remaining in the presence of the air-acid mixture for 200 minutes. The post-mortem examination showed no marked inflammation of the mucous membrane of the eyes, nose, or mouth, or œdema of the glottis. The bronchial passages were, however, hyperæmic, and the lungs exhibited œdema. S. B. S.

The Action on Man of Vapours of Technical and Hygienic Importance. XXXI. The "Nitrous Gases": Nitric Oxide. Nitrogen Dioxide, Nitrous and Nitric Acids. KARL B. LEHMANN and HASEGAWA (*Arch. Hygiene*, 1913, **77**, 323—368).—A summary is given of a number of cases in the literature describing the toxic symptoms produced in man by the "nitrous gases," which act essentially as a mixture of nitrous and nitric acid. Attention is called to the great differences as regards the susceptibility of

individuals to the poison. Experiments were carried out on animals with gas made by the action of nitric acid on copper. This was diluted with hydrogen, and mixed with air. An apparatus is figured to show how this was accomplished, and how samples of the air to which the animals were exposed could be removed for analysis. The analysis was accomplished by passing the air, first, over hydrogen peroxide, when the nitrous acid was oxidised to nitric acid, and the total nitrate, both preformed and produced by oxidation of the nitrous acid, was precipitated by nitron. The gas unabsorbed in the first absorption apparatus was passed through a second apparatus containing potassium iodide, and the iodine set free was titrated by thiosulphate solution. The general result of the experiments with mixtures of equimolecular proportions of nitrous and nitric acid is to show that the mixture acts as if all the nitrogenous products were in the form of nitric acid (see preceding abstract). In the majority of the animal experiments the toxic symptoms were different from those in man. These were generally only slight inflammatory reactions on the mucous membranes, œdema of lungs, in certain experiments, methæmoglobin formation, and indications of an action on the central nervous system. The temporary recovery after removal from the noxious vapours, with subsequent relapse, as is observed in the case of man, occurred only seldom in the case of animals. Experiments on man (Hasegawa), but carried out only with small doses of the noxious vapours, indicated that the symptoms were similar to those on animals. Various experiments were also carried out on the reduction of nitrate to nitrite by animal tissues, on the distribution of nitrites in tissues after injection into the trachæa, and on the toxic effect of nitrite administration. It was shown that the quantities of nitrite which produced severe symptoms after inhalation were far smaller than the quantities necessary to produce characteristic nitrite poisoning. The injurious effects in the inhalation experiments are to be ascribed to the production of the lung œdema. In man there is a latent period before the injurious effects are observed, which is generally absent in the case of animals.

S. B. S.

The Natural Resistance of the Hedgehog towards Certain Poisons. M. A. Willberg (*Biochem. Zeitsch.*, 1913, **48**, 157—174).—It was found that the hedgehog could tolerate a dose of atropine sulphate 248 times larger (calculated per kilo. of body-weight) than that tolerated by man. The tolerance towards morphine hydrochloride was 245 times as greater; towards nicotine, 29 times; towards potassium arsenite, 10 times; towards curare, 7 times; towards potassium cyanide, 6 times; towards mercuric chloride, 4 times; and towards phenol, twice as great. There was no difference in the tolerance towards strychnine nitrate. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Bacterial Reduction of Sulphates to Sulphides. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 165—169).—Sasaki and Otsuka (A., 1912, ii, 475), working with 21 races of bacteria in pure culture, were unable to reduce sulphate to sulphide, and further state that bacteria produce no hydrogen sulphide from taurine.

Positive evidence is now quoted showing that in a great variety of cases bacteria relatively readily reduce sulphates to hydrogen sulphide. E. F. A.

Bio-chemistry of Micro-organisms. VII. The Fermentation of Formic Acid by Bacillus Kiliense in a Medium of Constant Composition. HARTWIG FRANZEN and F. EGGER (*Zeitsch. physiol. Chem.*, 1913, **83**, 226—228).—The paper consists chiefly of data obtained from experiments carried out on the same lines as those in which *Bacillus prodigiosus* was used (A., 1912, ii, 669). A slight production of formic acid occurs during the early stages of growth, after which fermentation takes place. The results show great divergence in the behaviour of the organism in different series of cultures, and general conclusions cannot be drawn. H. B. H.

Action of Uranium Salts and Metallic Uranium on the Pyocyanic Bacillus. HENRI AGULHON and ROBERT SAZERAC (*Compt. rend.*, 1913, **156**, 162—164. Compare this vol., i, 143).—A study of the influence of uranium salts, soluble and insoluble, on the pyocyanic bacillus, the amount of pyocyanin formed being estimated colorimetrically, the culture medium used being hydrolysed serum. The toxic dose of uranyl acetate is 1 in 500, and of uranyl nitrate, 1 in 200. Doses of from 1 in 50,000 to 1 in 1000 are distinctly favourable, as was shown by the colour test, and also by the thickness of the microbic film produced. With insoluble uranium compounds, potassium or ammonium uranate, doses of 1 in 1000 to 1 in 100 gave an increase of 100% in the yield of pyocyanin, whilst in the case of the metal itself doses of 1% gave a decided growth within twenty-four hours in a medium to which the bacillus was not accustomed. The medium being neutral, this last effect could not be due to any of the uranium passing into solution, and finally favourable action was produced on the microbe in sealed tubes, the uranium being outside, thus pointing to the radioactivity of the uranium as being the cause of the increased growth in this and the previous cases. W. G.

Influence of Salts of Uranium and Thorium on the Development of the Tubercle Bacillus. PAUL BECQUEREL (*Compt. rend.*, 1913, **156**, 164—166).—Radioactive salts of uranium and thorium behave physiologically like many other non-radioactive salts. They each have an optimum dose, which produces the

maximum growth of the bacillus, above which they begin to exert a toxic effect, uranyl nitrate being much more toxic than thorium nitrate. A dose of 1 in 2500 of the former has a marked inhibitory influence, whilst the same dose of the latter seems to be its optimum as regards increased microbic growth. W. G.

Indole Reaction. HUGO ZIPFEL (*Centr. Bakt. Par.*, 1913, i, **67**, 572—584. Compare A., 1912, ii, 793).—The contradictory results often yielded by the indole test may be attributed to unsuitability or variability of the medium. The use of a composite tryptophan medium with or without the addition of glycerol or dextrose is recommended, whereby trustworthy results can be obtained in twenty-four to forty-eight hours. Comparative tests of a large number of strains of certain pathogenic and non-pathogenic bacteria were made, and consistent results obtained with the various strains of each species of organism. The *p*-dimethylaminobenzaldehyde test for indole was found to be the most trustworthy. H. B. H.

Mechanism of Alcoholic Fermentation. S. KOSTYTSCHEV (*Ber.*, 1913, **46**, 339. Compare Kostytschev, A., 1912, ii, 589; Kostytschev and Hübbenet, *ibid.*, 1912, ii, 860).—A claim for priority against von Lebedev (this vol., i, 144), in demonstrating that acetaldehyde is formed during the fermentation of sugar in the presence of zinc chloride, and, further, that acetaldehyde is reduced to ethyl alcohol by living yeast and various yeast preparations. H. W.

Alcoholic Fermentation. III. Conditions Regulating the Formation of Acetaldehyde during the Fermentation of Hefanol (Yeast). S. KOSTYTSCHEV (*Zeitsch. physiol. Chem.*, 1912, **83**, 93—104. Compare A., 1912, ii, 589; also Kostytschev and Hübbenet, A., 1912, ii, 860).—A reply to the criticisms of Neuberg and Kerb (A., 1912, ii, 973). Paracetaldehyde is very easily decomposed into acetaldehyde on distillation with traces of acid.

Autofermentation of yeast is a true alcoholic fermentation of the yeast glycogen; acetaldehyde is one of the products of the change. When fermentation of hefanol is effected in presence of sufficient methylene-blue to render the active reducing agent inoperative, acetaldehyde is formed as the normal reduction of acetaldehyde to ethyl alcohol is restricted. E. F. A.

Biochemical Synthesis of Alkylglucosides (α-Glucosides) by means of a Ferment (α-Glucosidase) contained in Air-dried Bottom Yeast. α-Ethylglucoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 168—170).—The authors have obtained α-ethylglucoside in a crystalline form, $[\alpha]_D + 150.64°$, by the action of a ferment, extracted from bottom yeast by water, on a dilute alcoholic solution of dextrose containing at least 65% of water by volume. The yield with respect to the dextrose used was 33%, and the glucoside was readily hydrolysed in aqueous solution by the same ferment, which they name α-glucosidase. W. G.

Assimilation of Nitrate and Nitrite. V. OSKAR BAUDISCH and ERWIN MAYER (*Ber.*, 1913, **46**, 115—125. Compare A, 1911, ii, 523; 1912, ii, 286, 1202).—When a dilute formaldehyde–potassium nitrate solution is exposed to sunlight a mixture of nitrous oxide and hydrogen, together with some carbon dioxide and monoxide, is evolved. In a formaldehyde–potassium nitrite solution, in addition, small quantities of nitric oxide are also formed. This originates from the decomposed nitroxyl NOH, a substance which does not exist as gas.

Angeli's salt, ONa·N:NO·ONa, decomposes on warming in aqueous solution into nitrous and nitric oxides and ammonia.

Solutions of potassium nitrite in either formaldehyde or methyl alcohol which have been exposed to light contain methylamine and, further, formic acid, hyponitrous acid, and hydroxylamine. In addition an alkaloidal compound similar to nicotine and containing a pyrrole ring is formed. Whereas in the assimilation of carbon the carbonic acid is reduced to carboxylic acid by the yellow and red rays of the spectrum, in the assimilation of nitrogen the blue, violet, and ultra-violet rays cause the reduction of nitrates to nitroxyl. E. F. A.

The Influence of Uranium and Lead on Vegetation. JULIUS STOKLASA (*Compt. rend.*, 1913, **156**, 153—155).—Uranyl nitrate added in small amounts to pot cultures of *Melilotus albus* already supplied with suitable fertilisers, had a favourable effect on the total yield of dry matter, the optimum quantity being 2·5 kilos. of uranium per hectare of soil. With 20 kilos. per hectare there was no indication of any toxic effect. The results with lead nitrate on oats and on *Polygonum fagopyrum* are of the same order, but the amount of lead which has an injurious effect is much less than in the case of uranium, the addition of lead nitrate at the rate of 8 kilos. per hectare being detrimental to the total crop in each case. W. G.

The Cause of Growth in Plants. I. G. A. BOROVIKOV (*Biochem. Zeitsch.*, 1913, **48**, 230—246).—The author reviews M. Fischer's experiments on the influence of acids, bases, and salts on various imbibition processes, for example, in gelatin and muscle. The view has been expressed by Fischer and others, that the phenomena of growth are determined, not so much by the osmotic properties of the cell, as by the capacity of the various colloids to imbibe water. The capacity is affected differently by various ions contained in the solution. The method of experiment employed by the author to investigate the various factors was as follows. Seedlings (six days old) of *Helianthus annuus* were placed in tubes which hung vertically in cylinders containing various solutions, and after intervals of three, six, and twelve hours and longer, removed, and the rate of growth was measured and compared with the rate of growth in pure water. The influence of various acids, bases, and salts on the rate of growth during short intervals was thus ascertained. It was found that acids accelerate the growth during the

first period, and if salts are present at the same time, the growth in the presence of both acid and salt is diminished as compared with that in acid alone. The effect of the various ions and cations was studied in some detail, and attention is drawn to the parallelism between their influence on the rate of growth and their general effect on imbibition processes. The experiments, generally, confirm the conception of the relationship between imbibition processes and growth. S. B. S.

Presence of Formaldehyde in the Sap of Green Plants. FRANCESCO ANGELICO and G. CATALANO (*Gazzetta*, 1913, **43**, i, 38—43). —The formaldehyde which is supposed to be an intermediate product in the photosynthesis of starch in green plants has never been demonstrated in the sap with certainty. The test for formaldehyde with atractylin (compare Angelico, A., 1910, i, 403) is not only very sensitive, but also specific. The leaf-sap and its distillate of eleven species of green plants tested in this way showed the presence of formaldehyde, whilst the same products from six species previously kept for twenty-four hours in the dark gave no reaction. Three non-chlorophyllic, parasitic plants were also tested, and formaldehyde was found to be absent. The results are therefore in complete agreement with the usual theory of photosynthesis.

R. V. S.

The Function of the Carboxylase in Plants. W. ZALESKI and ELIZABETH MARX (*Biochem. Zeitsch.*, 1913, **48**, 175—180).—The seeds employed were sterilised with mercuric chloride, then dried and powdered. The seeds of *Lupinus luteus* decompose free pyruvic acid as readily as they do its sodium salt. Pea seeds, on the other hand, decompose the free acid less readily than its salt, a fact due probably to the alkalinity of the powder. Seeds of *Vicia faba* only weakly attack the free acid, although they readily attack the sodium salt. Lupine seeds can also attack pyruvic acid in a vacuum. Both pyruvic acid and its sodium salts inhibit the carbon dioxide production of the immature seeds. Acetaldehyde could be detected in the experiments with both lupine and pea seeds when pyruvic acid was present. It could be also detected, but in very much smaller quantities in the control experiments, in which the acid was absent. The authors call attention to the parallelism of the actions of the seed carboxylase and of zymase, and discuss the rôle played by pyruvic acid in degradation of sugars and the production of ethyl alcohol. S. B. S.

Rôle of Oxydases in the Formation of the Anthocyan Pigments of Plants. FREDERICK KEEBLE and EDWARD FRANKLAND ARMSTRONG (*J. of Genetics*, 1912, **2**, 277—311. Compare A, 1912, ii, 73).—The methods previously described for the localisation of oxydases have been extended to a variety of plants. Peroxydase is shown to be more widely distributed than the organic peroxide which activates it. The very general phenomenon of browning presented by dried plants is regarded as an indication of the presence

of a complete oxydase. Exposure of plants to darkness leads to the formation of peroxide and to an increase of peroxydase. The bearing of these facts on the general metabolism in the plant is discussed.

E. F. A.

Colloidal Chlorophyll and the Shifting of the Absorption Bands in the Leaves of Living Plants. D. IVANOVSKI (*Biochem. Zeitsch.*, 1913, **48**, 328—331).—Herlitza has drawn the conclusion, from spectroscopic observations, that chlorophyll exists in the colloidal form in living plants. The author gives a table of extinction coefficients, and shows that those of the chlorophyll of the leaf fall between those of colloidal chlorophyll and of an alcoholic solution of the pigment. He draws attention to the fact that the chlorophyll in leaves exists, not evenly distributed, but in the chloroplasts, and that the absorption spectrum of the leaf combines the characters of an absorption and reflection spectrum. He shows that the absorption spectrum of the leaf can be closely imitated by the addition of electrolytes to colloidal chlorophyll. According to the size of the granula thus produced, the absorption band is shifted thereby towards the ultra-red. S. B. S.

Plant Fats. CARL THOMAE (*J. pr. Chem.*, 1913, [ii], **87**, 144).—The fatty and waxy constituents of yeast, rose blossoms, and the skins of apples, grapes, peaches, potatoes, lemons, gherkins, and other parts of plants may be readily isolated in a state of purity by heating under diminished pressure. F. B.

The Non-Specificity of Zinc as a Biological Catalyst for the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 258—261).—The author has tried the effect of replacing the zinc in Raulin's solution by cadmium on the cultivation of *Sterigmatocystis nigra*, and his results are not in accord with those recently put forward by Javillier (compare this vol., i, 235). On the contrary, he finds that cadmium replaces zinc perfectly in Raulin's solution, and, like it, plays a very energetic part in the rapid growth of the plant, being fixed by the plant. Further, he finds that zinc is not a specific catalyst for this culture, but can be replaced by other elements chemically analogous to it.

W. G.

Attempts to Substitute Glucinum for Magnesium and Zinc in the Culture of Sterigmatocystis nigra (Aspergillus niger). MAURICE JAVILLIER (*Compt. rend.*, 1913, **156**, 406—409. Compare this vol., i, 235).—A reply to Lepierre (preceding abstract). From further experiments the author maintains that glucinum cannot replace magnesium or zinc in the culture medium for *Aspergillus niger*, the magnesium being necessary as a nutrient and the zinc as a catalyst. He suggests that the difference between his and Lepierre's results may be due to the conditions of their culture media, or hereditary influences on the cultures. W. G.

Replacement of Zinc by Glucinum in the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 409—411. Compare this vol., i, 235; preceding abstracts).—The results obtained are in direct opposition to those of Javillier (previous abstract). The author finds that the zinc in Raulin's liquid can be replaced by glucinum without affecting the weight of crop finally obtained from the culture of *Aspergillus niger* thereon, except that the maximum is somewhat retarded. This retardation is, however, only relative, and diminishes as the plant adapts itself to the new medium. Time, adaptation, and easy access of air play an important part in these cultures. The glucinum is fixed by the plant. W. G.

Formation of Urea by Two Moulds. ROBERT FOSSE (*Compt. rend.*, 1913, **156**, 263—265. Compare A., 1912, ii, 1203).—The author has isolated urea in small quantities in the form of its xanthhydrol derivative from the expressed juice of mycelium gathered from the surface of Raulin's liquid and also from *Aspergillus niger* grown on a solution in which ammonium nitrate has replaced the chloride in Raulin's liquid. *Penicillium glaucum* similarly contains small quantities of urea in its cells. From his results the author draws the conclusion that the principal factor in ureogenesis is a process of oxidation, and not, as at present supposed, a diastatic oxidation. W. G.

The Nitrogenous Constituents of Lime Juice. CASIMIR FUNK (*Biochem. J.*, 1913, **7**, 81—86).—In view of work on beri-beri, in which the physiological importance of certain substances (probably pyrimidine derivatives) has been shown, lime juice was examined in reference to scurvy. Lime juice cures scurvy, and also contains an antineuritic substance. Pyrimidine substances in general prolong life in birds with polyneuritis. No anti-scorbutic substance, however, was separated out from lime juice. The investigation was hampered by the guinea-pigs refusing to take oats, a diet which leads to scurvy in these animals. Milk prevents oats from causing scurvy, even though the proteins are removed. The anti-scorbutic material in milk is destroyed by a high temperature. Its unstable character may have led to the negative results with lime juice. Several new compounds were, however, separated from lime juice; one, $C_{18}H_{24}O_3$, needles, m. p. 97—100°, apparently belongs to the terpene group; one, $C_6H_7O_2N_5$, crystalline plates, m. p. 282° (corr.), to the purine group; one, $C_9H_{18}O_6N_2$, microscopic spherolites, m. p. 188—189° (decomp.), to the pyrimidine group; and a fourth to the choline group; the latter crystallised in cubes, and gave a platinichloride, $(C_8H_{15}O_2N)_2H_2PtCl_6$, m. p. 220°. The phosphotungstic and silver nitrate precipitates were mainly examined. W. D. H.

Constituents of Apples. CARL THOMAE (*J. pr. Chem.*, 1913, [ii], **87**, 142—144).—The substance, m. p. above 200°, previously isolated by the author (A., 1911, ii, 920) from apple-skins may be separated

by treatment with ether into an insoluble substance of high melting point, and a waxy substance crystallising in needles, m. p. 68·5°. On distillation under diminished pressure, the oil obtained by extracting the skins with ether yields a crystalline substance of low melting point having an odour of apples and a yellow oil which readily solidifies. The behaviour of the skins on distillation is also described. F. B.

Leaves of Barosma venusta. HAROLD R. JENSEN (*Pharm. J.*, 1913, [iv], **36**, 60—61).—This material from Cape Province, South Africa, yielded 1·1% of volatile oil, $D_{15·5}^{15·5}$ 0·8839, $\alpha_D^{20}+0°30'$, n_D^{20} 1·4967, of greenish-yellow colour, and having acid value 2·4 and saponification value 13·4. On treatment with potassium hydroxide solution, 16% of the oil dissolved, and a further 4% was absorbed by a solution of neutral sodium sulphite. The oil was separated into nine fractions by distillation under reduced pressure, and the physical constants, ultimate composition, and reactions with bromine, sodium, and phenylhydrazine of each fraction are recorded. From a consideration of these data the following composition is tentatively suggested for the oil: myrcene, 35; chavicol, 16; myrcenol and sesquiterpene alcohols, 15; methylchavicol and anethole, 15; sesquiterpenes, esters, ketones, aldehydes, and acids, 19%. The leaves also contain oleoresin, acid resins, colourless glucosides, fat, carbohydrates, and a little tannin. The results show that these leaves do not contain the same constituents as the commercial buchus derived from *B. betulina* and *B. serratifolia*, and that they cannot be used in medicine in place of these. T. A. H.

Constituents of Lycoperdon bovista. JAN J. BLANKSMA (*Chem. Weekblad*, 1913, **10**, 96—100).—Fresh specimens of the edible mushroom, *Lycoperdon bovista*, contain trehalose, tyrosine, a substance with m. p. 165°, chitin, and leucine, all previously isolated (compare Bourquelot, *J. Pharm. Chim.*, 1907, [vi], **25**, 382; Bamberger and Landsiedl, A., 1903, ii, 567; 1905, ii, 852). The trehalose is converted by trehalase, invertase, and diastase into reducing sugars, these ferments being present in the mushrooms. The darkening in colour of mushrooms is explained by the conversion of tyrosine into melanin, a black substance, under the influence of tyrosinase. It is possible that leucine is converted into *iso*amylamine, and the tyrosine into *p*-hydroxylphenylethylamine, a substance of very poisonous character. It is known that old specimens of *Lycoperdon bovista* are poisonous. The author recommends the preparation of glucosamine hydrochloride by boiling mushrooms with dilute hydrochloric acid after elimination of proteins, fats, and calcium salts. A. J. W.